VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ
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PREKONCENTRAČNÍ TECHNIKY PRO STANOVENÍ PLATINOVÝCH KOVŮ V ŽIVOTNÍM PROSTŘEDÍ

Habilitační práce
v oboru Chemie a technologie ochrany životního prostředí

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Poděkování

Chtěla bych touto cestou poděkovat všem mým blízkým a známým. Na prvním místě bych ráda poděkovala celé mé milované rodině, zejména mému manželovi a dcerám, kteří jsou mojí velkou oporou a každodenní motivací. Až s příchodem mých dětí na svět jsem si mnohé věci uvědomila a řadu z nich přehodnotila.

Další nezměrný dík patří mému učiteli, vedoucímu disertační práce, příteli a osobnosti, které si budu v odborné komunitě vážit vždy ze všech nejvíc, profesorovi Lumíru Sommerovi. To on mne zasvětil do krás vědecké práce. Naučil, jak „analyticky“ myslet, inspiroval mne nekonečnými nápady, spolu jsme publikovali moje první výsledky a to on mi předal své zkušenosti, názory a pohled nejen na vědu, ale i život jako takový. A přesně tak se to snažím předávat i já dalším generacím studentů. Když v roce 2014 opouštěl Fakultu chemickou, slíbila jsem mu, že na svém vědeckém růstu budu pracovat dál. Letos nás opustil všechny († 2. 4. 2019), a tímto bych mu také ráda tuto habilitační práci věnovala.

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ABSTRAKT

Platinové kovy vstupují do životního prostředí především prostřednictvím celosvětového masivního používání autokatalyzátorů, ve kterých svým katalytickým účinkem snižují emise oxidu uhličitého, oxidů dusíku a uhlovodíků. Platinové kovy se mohou během provozu automobilů uvolňovat z katalyzátorů ve formě mikročástic a nanočástic, v elementární formě, případně ve formě povrchově oxidovaných částic. Významným zdrojem platinových kovů v životním prostředí je také využití biologicky aktivních sloučenin platinových kovů v onkologické terapii, kdy se po léčbě stávají součástí odpadních vod. Platinové kovy vstupují a pohybují se tak ve všech složkách životního prostředí a podléhají také dálkovému transportu. Stále se však v životním prostředí vyskytují ve velmi nízkých koncentracích. Jejich přímé stanovení je často obtížné, možné pouze za použití vysoce citlivých analytických technik. Před jejich vlastním stanovením je často nezbytný prekoncentrační krok ke zvýšení jejich koncentrace na měřitelnou hodnotu. Tato habilitační práce se zabývá výzkumem, vývojem a inovacemi prekoncentračních technik metodou extrakce do tuhé fáze a aplikací těchto prekoncentračních technik při hodnocení znečištění jednotlivých složek životního prostředí. Současný výzkum směřuje k objasnění chování nanočástic platinových kovů v environmentálních systémech a zjištění jejich vlivu nejen na biologické systémy, ale také na fyzikálně-chemické parametry neživých složek životního prostředí.

KLÍČOVÁ SLOVA

platinové kovy; nanočástice; autokatalyzátory; prekoncentrace; SPE; AAS; environmentální vzorky

ABSTRACT

Platinum group metals enter the environment primarily through the worldwide massive use car catalyst where their catalytic action reduces emissions of carbon dioxide, nitrogen oxides and hydrocarbons. The platinum group metals can be released during operation of the automobile catalysts in the form of micro-particles and nanoparticles, in elemental form or in the form of surface-oxidized particles. An important source of platinum group metals in the environment is also the use of biologically active compounds of platinum group metals in oncological therapy, when they become part of wastewater after treatment. Platinum group metals enter and move in all environmental compartments and are also subject to long-distance transport. However, they still occur at very low concentrations in the environment. Their direct determination is often difficult, using only highly sensitive analytical techniques. Prior to their determination, a preconcentration step is often necessary to increase their concentration to a measurable value. This habilitation thesis deals with the research, development and innovations of preconcentration techniques using the solid phase extraction method and their application in the evaluation of pollution of individual components of the environment. Recent research is aimed at identifying the behavior of platinum metal nanoparticles in environmental systems and their impact not only on biological systems but also on physico-chemical parameters of non-living environmental components.

KEYWORDS

platinum group metals; nanoparticles; preconcentration; SPE; autocatalyst; AAS; environmental samples

OBSAH

1 ÚVOD

Cílem této habilitační práce je přehledně zmapovat problematiku platinových kovů, které se věnuji již více než 20 let. V devadesátých letech 20. století to byla problematika zcela nová a neprobádaná. S masivním používáním autokoatalyzátorů však začalo přibývat studií zabývajících se stanovením platinových kovů a vývojem metod pro jejich prekoncentraci a také aplikací těchto technik při analýze vzorků z životního prostředí. V současné době, více než 25 let po zavedení autokatalyzátorů jako povinné výbavy automobilů v ČR, je toto téma stále aktuální. Důkazem toho jsou neustále nové publikované studie o problematice platinových kovů. I přes to však dosud neexistují jednoznačné informace o jejich toxicitě v jednotlivých složkách životního prostředí, není přesně známo jejich chování v environmentálních matricích a nejsou přesně kvantifikovány jejich jednotlivé chemické formy a sloučeniny vznikající za environmentálních podmínek.

Můj přínos k této problematice je v této habilitační práci shrnut a rozdělen do několika tematických okruhů. Úvodní kapitola byla sepsána zejména pro pochopení širších souvislostí globálního charakteru i některých mezinárodních ekonomických aspektů. Kapitoly **Prekoncentrační techniky**, **Platinové kovy v životním prostředí** a kapitola **Nanočástice platiny** vždy obsahují podkapitolu se zhodnocením současného stavu a aktuálních poznatků a podkapitolu se zhodnocením mého přínosu v této oblasti. Dohromady tak tvoří ucelený přehled všech informací o platinových kovech, jejich stanovení včetně prekoncentračních technik a aplikací pro využití při analýzách reálných vzorků. V kapitole **Závěry a vize do budoucna** je nastíněno jakým směrem se pravděpodobně bude ubírat další výzkum v této oblasti. Jsou zde také zmíněny některé alternativní koncepce v automobilové dopravě, které by v budoucnu mohly významně ovlivnit používání platinových kovů v automobilových katalyzátorech, a tím mít také poměrně zásadní vliv na jejich antropogenní vstupy do životního prostředí.

2 GLOBÁLNÍ ASPEKTY STUDOVANÉ PROBLEMATIKY

Všechny platinové kovy (ruthenium, rhodium, palladium, osmium, iridium a platina) se přirozeně vyskytují v zemské kůře ve velmi nízkých koncentracích. Tyto kovy a jejich sloučeniny jsou velmi vzácné a jejich obsahy se pohybují řádově v desetinách $ng.g^{-1}$ horniny, s výjimkou ojedinělých nalezišť, kde jejich koncentrace narůstá na 1 000 až 10 000 násobek těchto hodnot. Mohou se nacházet ryzí, rozptýleny v říčních rýžovištích nebo vázány v podobě arsenidů a sulfidů v rudách obsahujících zejména Ni, Cu a Fe [1]. Na rozdíl od ostatních přechodných kovů se platinové kovy vyskytují v přírodních zdrojích často v elementární podobě, s výskytem difuzního charakteru.

Platinové kovy se v současnosti používají v mnoha moderních technologiích a výrobcích. Jejich spotřeba neustále narůstá (z 90 000 t v roce 2010 na 106 000 t v roce 2015). Jejich přírodní rezervy a zdroje se však nachází zejména v Africe [2]. Řadí se tak mezi „kritické“ kovy, protože jejich poptávka pro průmysl může být ovlivněna spolehlivostí dodávek v důsledku sociálně-ekonomických aspektů, spíše než z hlediska vyčerpání přírodních zdrojů [3]. Aktuální se tak stává také téma recyklace vzácných prvků z elektronického odpadu a použitých katalyzátorů [4].

Alarmující je však antropogenní vstup těchto kovů a jejich sloučenin do životního prostředí [5]. Platinové kovy, zejména platina, palladium a rhodium, se díky jejich masivnímu využívání v automobilovém průmyslu za poslední tři desítky let staly významným zdrojem antropogenního vstupu těžkých kovů do životního prostředí. Tyto prvky jsou hlavními komponentami automobilových katalyzátorů, mají zde velmi významnou a nenahraditelnou funkci. Podílejí se na eliminaci toxických sloučenin vznikajících spalovacím procesem. Během provozu automobilu se však i tyto prvky uvolňují a stávají se součástí automobilových emisí. Výfukové plyny obsahují zejména směs oxidu uhelnatého a oxidů dusíku, uhlovodíky a také některé produkty nedokonalého spalování, např. aldehydy, ketony, polycyklické aromatické uhlovodíky nebo karboxylové kyseliny. Platinové kovy snižují obsah těchto polutantů na takové koncentrační hladiny, aby byly splněny požadované emisní normy. Jelikož se tyto normy neustále zpřísňují, je používání platinových kovů v dnešní době nezbytné. Z počátku byly snahy snižovat vznik toxických zplodin úpravou motorů, ale katalytické systémy se ukázaly jako nejefektivnější. V České republice platí od roku 2017 emisní norma EURO 6,2. V roce 2020 ji nahradí norma EURO 6,3 a dále je plánováno zavedení normy EURO 7. Ta však svými požadovanými limity pravděpodobně urychlí vývoj vozidel s alternativním pohonem.

Přirozený koloběh platinových kovů je díky jejich nízké reaktivitě, malé rozpustnosti a mobilitě velmi omezen, ale antropogenním vstupem z automobilových emisí značně narušen. Emise těchto kovů a jejich sloučenin jsou největší v okolí dopravních komunikací s vysokou hustotou dopravy, nadlimitní pak v místech se špatnými rozptylovými podmínkami (např. tunely, podjezdy atd.). Tato kontaminace však nemá jen lokální dopad. V případě platinových kovů, zejména platiny, byl prokázán dálkový transport těchto látek, a tím potvrzeno globální znečišťování celé planety [6].

Pravděpodobně velké riziko zvyšujících se koncentrací platinových kovů v jednotlivých složkách životního prostředí nelze objektivně posoudit v důsledku doposud nedostatečných a nekompletních informací o jejich toxicitě, možné bioakumulaci, negativních vlivech na zdraví člověka i jednotlivé organismy v životním prostředí. Vliv platinových kovů byl doposud popsán v několika málo studiích, např. [7-12]. Dokonce ani Světová zdravotnická organizace WHO nemá o chování těchto kovů a jejich sloučenin v životním prostředí dostačující informace, pouze částečné o platině [13] a palladiu [14]. Chování a osud rhodia a jeho sloučenin v životním prostředí je téměř neznámé.

Dalším významným zdrojem těchto kovů v životním prostředí jsou odpadní vody onkologických léčebných zařízení [15-16]. Platinové kovy, zejména pak sloučeniny platiny, ale nově i palladia [17-18] a rhodia, jsou ve formě některých svých komplexních sloučenin velmi účinnými cytostatiky. Po účinné léčebné reakci v těle pacienta dochází k následnému vyloučení z těla. Kontaminované odpadní vody, které jsou z hlediska obsahu těchto farmak často neúčinně čištěny v čistírnách odpadních vod, se tak stávají bodovými zdroji sloučenin těchto kovů. Jejich odstranění je možné jen za použití speciálních technik [19]. Tato protinádorová metalofarmaka se zde vyskytují ve formách rozpustných, biologicky dostupných a zejména biologicky značně aktivních [20]. Velmi často jsou jejich cytostatické vlastnosti doprovázeny vlastnostmi silně toxickými pro živé organismy [21-22], s prokázaným karcinogenním účinkem a velmi nízkou biodegradabilitou.

Antropogenními vstupy tak dochází ke globální kontaminaci všech složek životního prostředí. Prioritními vstupy jsou automobilové emise a odpadní vody. Platinové kovy a jejich sloučeniny pak prostupují do všech živých a neživých složek. Byly nalezeny v polétavém prachu [23-24], silničním prachu [25], půdách [26-27], vegetaci [28-29], v odpadních vodách [19], [30], v říčních vodách [20], akvatických organismech a sedimentech [31-32], v tělech živočichů na vyšších stupních potravního řetězce [33] i v lidském těle [34-35].

Z výše uvedených skutečností je patrné, že téma platinových kovů se dotýká každého z nás. Jejich problematika je celosvětová, ať už z hlediska zdrojů, využití v automobilovém průmyslu, aplikacích v lékařství, v chemickém průmyslu, ale i z pohledu nakládání s odpady a kontaminace celého životního prostředí z lokálního i globálního pohledu. Moje vědecká práce se snaží přispět k objasnění stavu a míry kontaminace jednotlivých složek životního prostředí výzkumem a inovacemi v oblasti analytické a environmentální chemie platinových kovů.

3 PREKONCENTRAČNÍ TECHNIKY

3.1 SOUČASNÝ STAV PROBLEMATIKY PREKONCENTRACE PLATINOVÝCH KOVŮ

Platinové kovy se, i přes výše uvedené antropogenní zdroje, vyskytují ve většině složek životního prostředí stále ve velmi nízkých koncentracích. Často nelze tak nízké koncentrace stanovit přímo a/nebo je k jejich stanovení nutné použít nejcitlivější analytické techniky s velmi nízkým limitem detekce (LOD) a limitem stanovitelnosti (LOQ). Mezi tyto techniky se řadí zejména metoda hmotnostní spektrometrie s indukčně vázaným plazmatem (ICP-MS) [36]. Nákup a provoz těchto přístrojů je mnohdy finančně velmi náročný [37]. Proto byly studovány, testovány a inovovány sorpční techniky pro nabohacení nízkých koncentrací platinových kovů na hodnoty měřitelné běžnějšími a provozně levnějšími technikami, jako jsou metody atomové absorpční spektrometrie s elektrotermickou atomizací (ET-AAS) a atomové emisní spektrometrie s indukčně vázaným plazmatem (ICP-OES).

Jednou z nejefektivnějších metod zakoncentrování platinových kovů je metoda extrakce do tuhé fáze, neboli SPE (Solid Phase Extraction). Existuje celá řada sorbentů, ať už běžně dostupných, selektivních nebo specifických, které se k tomuto účelu používají. Výhodou této techniky není jen zvýšení koncentrace vybraných prvků na měřitelnou hodnotu, ale také jejich současná separace od samotné matrice vzorku, která mnohdy vlastní analytické stanovení ruší [38]. Velmi významnými parametry při testování a výběru vhodného sorbentu jsou nejen jeho selektivita, specifičnost, sorpční a eluční účinnost a možnost opakovaného použití, ale také jeho cena, dostupnost na trhu, spotřeba chemikálií a organických rozpouštědel použitých při sorpčním procesu, vliv možných interferencí na průběh sorpce, použitelnost při analýze reálných matric a množství a druh vznikajícího chemického odpadu. Významnou roli tedy hraje i ekonomicko-ekologický aspekt vyvinuté metodiky prekoncentrační techniky platinových kovů.

Metoda SPE je separační metoda, jejímž principem je několik po sobě jdoucích kroků. SPE může být experimentálně prováděna ve statickém nebo dynamickém uspořádání. Při statické sorpci je k roztoku vzorku přidána navážka sorbentu a roztok se sorbentem je po určitou dobu protřepáván. Po oddělení sorbentu a analyzovaného roztoku je následně analyzováno množství analytu zachycené na sorbentu, ať už analýzou roztoku po sorpci nebo analýzou zachyceného analytu po eluci ze sorbentu. Při dynamickém uspořádání sorpce je sorbent umístěn v kolonce, kterou za určité průtokové rychlosti protékají roztoky pro kondicionaci sorbentu, analyt a v poslední fázi eluční činidlo. Průtoková rychlost roztoku kolonkou je optimalizována jednak z pohledu účinnosti sorpce, ale také z hlediska doby sorpce. Rychlost průtoku roztoků kolonou se sorbentem by měla být dostatečně nízká, aby docházelo k účinné sorpci, ale také dostatečně vysoká, aby se zbytečně neprodlužovala doba analýzy.

Při dynamické sorpci dochází v první fázi sorpce k přípravě sorbentu, tedy jeho kondicionaci vhodnými rozpouštědly (pro zlepšení účinnosti sorpce) nebo činidly (pro zvýšení selektivity sorpce). Během tohoto kroku dochází ke smáčení sorbentu, solvataci funkčních skupin sorbentu, aktivaci sorbentu a jeho funkčních skupin, popř. k navázání vybraných činidel na sorbent. Při volbě kondicionačního činidla musí být zohledněn typ pevného sorbentu a rozpouštědlo, ve kterém je rozpuštěn vzorek. Po kondicionaci sorbentu se musí dbát na to, aby sorbent nevyschl, mohlo by tak dojít ke snížení retenční kapacity daného sorbentu.

Následuje druhá fáze – sorpce analytu z roztoku vzorku. Vzorek může být na sorbent nanášen několika způsoby – samovolným protékáním roztoku pomocí gravitace, čerpáním roztoku vzorku pomocí peristaltické pumpy s přesně nastavenou průtokovou rychlostí, pomocí vodní vývěvy s nastavením podtlaku nebo kombinací peristaltického čerpadla a vakuového systému.

Třetí krok zahrnuje fázi, ve které by mělo dojít k úplnému odstranění sorbovaného roztoku vzorku ze sorbentu, popř. zachycených nečistot a interferentů. To může být provedeno promytím sorbentu vhodným rozpouštědlem o nízké eluční síle, které vyplaví zbytky matrice a interferentů, ale analyt zůstane na sorbentu pevně vázán. Kolonka se sorbentem se pro odstranění zbytků sorbovaného roztoku může také jen prosát vzduchem.

Poté následuje poslední, čtvrtá fáze - eluce nasorbovaného analytu vhodným objemem elučního činidla o dostatečné eluční síle. Vyeluovaný roztok se jímá a později přímo nebo s předúpravou analyzuje. Volba elučního činidla je velmi důležitá. Eluční činidlo může ovlivnit celkovou účinnost sorpce i její selektivitu. Při optimalizaci sorpčního postupu musí být zohledněno také to, jaká bude koncová detekce analytu. Během sorpce musí být použity takové chemikálie, aby nebylo rušeno vlastní stanovení jejich přítomností v analyzovaném roztoku eluátu. Popřípadě musí být tento eluát před vlastní analýzou upraven, např. odpařením organických rozpouštědel, s následným rozpuštěním odparku, nejčastěji ve vodných roztocích kyselin.

Mechanismus sorpce platinových kovů závisí jednoznačně na typu sorbentu a může probíhat různými fyzikálně-chemickými interakcemi, jako je adsorpce na povrchu sorbentu, vazba vznikem chelátu analytu, tvorbou a vazbou vzniklého iontového páru nebo iontovou výměnou. Volbou vhodného sorbentu s vysokou afinitou ke stanovovanému analytu lze zajistit účinnou, efektivní sorpci s vysokou selektivitou, popř. se specifickou afinitou k vybraným platinovým kovům. Pro tento účel lze využívat selektivních a specifických reakcí za tvorby komplexů nebo iontových párů s vybranými organickými činidly.

Při adsorpčním mechanismu sorpce je analyt na pevnou fázi vázán van der Waalsovými silami nebo hydrofobními interakcemi. Tyto hydrofobní interakce se uplatňují zejména u vysoce nepolárních sorbentů, tedy sorbentů s reverzní fází. Nejběžnějšími sorbenty tohoto typu jsou silikagely modifikované uhlovodíkovým řetězcem nebo vybranými organickými funkčními skupinami. Další velkou skupinu sorbentů tvoří polymerní sorbenty na bázi kopolymeru styrenu a divinylbenzenu. Eluce jsou v tomto případě prováděny organickými rozpouštědly, jako je methanol, etanol nebo acetonitril. Platinové kovy se však v roztoku nachází nejčastěji v podobě svých halogenokomplexů, přímá sorpce na tento typ sorbentů tedy neprobíhá. Iontové formy platinových kovů musí zreagovat s vhodným organickým činidlem a vzniklá komplexní forma je pak na sorbent poutána právě hydrofobními interakcemi nebo tento sorbent musí být modifikován tímto organickým činidlem.

Vznik chelátu analytu s vhodným organickým chelatačním činidlem, které obsahuje ve své molekule heteroatom, lze využít pro selektivní sorpci platinových kovů. Významnou afinitu k platinovým kovům mají zejména heteroatomy dusíku (funkční skupiny nitro-, amino-, imido- a azo-) a síry (nejčastěji funkční skupina thio-). Nejdůležitějšími požadavky pro efektivní a vysoce účinnou sorpci je selektivita činidla, stabilita vzniklého chelátu, dostatečně rychlá kinetika tvorby chelátu (v případě zachycení činidla na sorbentu musí protékající analyt reagovat s modifikovaným sorbentem dostatečně rychle), dobrá rozpustnost vzniklého chelátu ve vodě, popř. ve směsi vody a organického rozpouštědla, a dostatečně pevná vazba vzniklého chelátu na povrchu sorbentu [38].

Pokud nepolární sorbent modifikujeme iontově-párovým činidlem, naváže se svojí nepolární částí na nepolární sorbent hydrofobními silami a svojí polární částí vytváří iontový pár s ionty nebo komplexy analytu v roztoku. Typickými představiteli iontově-párových činidel vhodných pro prekoncentraci platinových kovů jsou kvartérní amoniové soli.

Při iontově-výměnné sorpci bývají využity takové sorbenty, které obsahují aniontové nebo kationtové funkční skupiny. Tyto skupiny mohou být navázány na sorbentu typu modifikovaného silikagelu nebo častěji na polymerních sorbentech typu kopolymeru styrenu a divinylbenzenu. K výměně iontů pak dochází mezi analyzovaným roztokem a pevným sorbentem. Iontoměničové skupiny mohou být silně nebo slabě disociovány a od toho se pak odvíjí jejich použitelnost v různé oblasti pH. Silně disociované skupiny jsou použitelné v celém rozsahu pH, zatím co slabě disociované skupiny pouze při pH vyšším než je jejich pK_a (disociační konstanta). Mezi silně kationtově-výměnné skupiny patří sulfonové skupiny a silně aniontově-výměnné kvartérní amoniové soli. Slabými kationtoměniči jsou karboxylové skupiny a slabými aniontoměniči ternární aminy [39].

Velmi zajímavou oblastí z hlediska prekoncentrace platinových kovů je využití mikroextrakce. Výhodou mikroextrakčních technik je minimalizace použitého množství organických činidel a jejich nahrazení ekologičtějšími alternativami. To zahrnuje zejména použití iontových kapalin (ILs, Ionic Liquids), jež jsou nazývány jako „rozpouštědla 21. století“ [40]. Iontové kapaliny jsou látky, které se skládají z organického kationtu a anorganického nebo organického aniontu, s teplotou tání pod 100°C. Nejzajímavější jsou pak iontové kapaliny kapalné již při laboratorní teplotě (RTILs, Room-temperature Ionic Liquids). Hlavními výhodami IL jsou nulová tenze par, termostabilita, vynikající solvatační vlastnosti, nehořlavost a nízká toxicita. Iontové kapaliny mají klíčovou roli v mikroextrakčních analytických technikách používaných pro prekoncentraci platinových kovů z environmentálních a biologických vzorků. Při mikroextrakčních postupech byl využit např. 1-hexyl-3-methylimidazol-2-thion [41] nebo 1-alkyl-3-methylimidazol chlorid [42].

Významnější pozornost začala být platinovým kovům věnována na konci 90. let minulého století. Důvodem bylo zavedení automobilových katalyzátorů s obsahem platinových kovů do povinné výbavy každého automobilu (ČR, 1. 1. 1993). To bylo prvotním signálem pro vývoj nových analytických postupů pro stanovení ultrastopových koncentrací těchto kovů. Prekoncentrační techniky tedy řešily základní problém těchto analytů v reálných vzorcích – jejich zakoncentrování na měřitelnou koncentrační hladinu. Podrobný přehled používaných prekoncentračních technik pro stanovení stopových množství platinových kovů prezentuje přehledná práce [43], **Příloha 1**. Jsou zde popsány metody stanovení platinových kovů, jejich předúprava před vlastním analytickým stanovením a zejména je tato práce zaměřena na přehled používaných prekoncentračních technik. Je zde popsáno využití různých typů sorbentů, používaných v problematice platinových kovů, jako jsou hydrofobní sorbenty s povrchově imobilizovanými komplexačními nebo chelatačními činidly, komplexující a chelatující sorbenty, vláknité komplexující sorbenty, sorbenty potažené kapalnými aniontoměniči a extrakčními činidly i základní aniontoměničové sorbenty.

Tabulka 1 pak přehledně zobrazuje možné SPE techniky využívané pro sorpci platinových kovů. Jsou zde uvedeny druhy a typy sorbentů, použitá modifikační činidla, analyty, podmínky eluce a použité koncové detekční techniky. Z **Tabulky 1** je zřejmé, že největší skupinu sorbentů využívaných pro prekoncentraci platinových kovů jsou modifikované hydrofobní sorbenty, zejména modifikované kopolymery styrenu a divinylbenzenu a modifikovaný silikagel. Druhou velkou skupinou jsou různé varianty aniontoměničových sorbentů.

Tabulka 1 Příklady sorbentů, používaných pro SPE platinových kovů

Sorbent	Analyt	Eluent	Detekce	Literatura
Modifikované hydrofobní sorbenty				
CMDCT na XAD-4	Pd, Pt, Rh	5 mol.l^{-1} NH_3	ICP-OES	[44]
Amberlite XAD 2 Amberlite XAD 4	Pd, Pt	acetonitril	ICP-OES	[45]*
Metalfix-Chelamin	Pt, Pd	0,5 mol.l^{-1} TU v 12 mol.l^{-1} HCl	ICP-OES	[46]
PAN-TU-GA	Pt, Pd	0,5 mol.l^{-1} TU v 0,5 mol.l^{-1} HCl	FTIR, X-ray	[47]
Strata SDB-L® modifikace: APDC, TU, PAR, 8HQS, Zephyramin®, Septonex®, Ajatin®	Pt, Pd, Rh, Ru, Os, Ir	acetonitril:HCl 4:1	ICP-MS	[48]*
MetaSep AnaLig®	Pd, Pt	1:0,5 TU:HCl	LEP-OES	[49]
Modifikovaný silikagel				
Bond-Elut C18®/Septonex®	Pt	acetonitril	ET-AAS	[23]*

StrataC18-E$^{®}$/ Septonex$^{®}$				
Bond-Elut C18$^{®}$/Septonex$^{®}$	Pt, Pd	acetonitril	ET-AAS	[25]*, [28]*
Separon$^{®}$ SGX C18	Pt, Pd, Rh, Ru, Os, Ir	Ethanol	ICP-OES	[50]*
Separon$^{®}$ SGX C18 Separon$^{®}$ SGX RPS Separon$^{®}$ SGX phenyl modifikace: Septonex$^{®}$, Sterinol$^{®}$, TTAB, CTAC, CPC	Pt, Pd, Rh, Ru, Os, Ir	ethanol methanol propan-2-ol aceton acetonitril	ICP-OES	[51]*
DPTH-gel	Pt	2 mol.l^{-1} HNO$_3$	ET-AAS	[52]
DMG SG	Pd	1 mol.l^{-1} v acetonu	ET-AAS	[53]
PAMAM SG	Pd	0,2% TU	FAAS	[54]
DPTH-gel	Pd	4 mol.l^{-1} HCl	ET-AAS	[55]
DKTS APSG	Pd	TU v HCl	FAAS	[56]
SAX sorbent	Pt, Pd	2 mol.l^{-1} v 1,2 mol.l^{-1} HCl	ICP-MS	[57]
SBA-15	Pt	TU	ET-AAS	[58]
SBA-15	Pd	0,6 mol.l^{-1} TU	ET-AAS	[59]
Bond-Elut C18$^{®}$/DMG QuadraSil™ TA	Pd	1 mol.l^{-1} v ethanolu 0,05 mol.l^{-1} TU	ET-AAS	[60]*
Aniontoměniče				
Separon$^{®}$ SGX AX	Ir, Pd, Pt	1 mol.l^{-1} HCl 5 mol.l^{-1} HNO$_3$	ICP-OES	[45]*
Amberlite® IRA-68 Amberlite® IRA-93 Amberlite® IRA-400	Pt, Pd, Rh	4 mol.l^{-1} HCl	ICP-OES	[61]
Dowex$^{®}$ 1-X8	Pt, Pd, Rh, Ir, Ru	0,3 mol.l^{-1} TU v 0,1 mol.l^{-1} HCl	ICP-OES ICP-MS	[62]
Dowex$^{®}$ 1-X10	Pt	0,1 mol.l^{-1} v 0,1 mol.l^{-1} HCl	ICP-OES	[63]
PSTH Dowex$^{®}$ 1-X8	Pt	2 mol.l^{-1} HNO$_3$	ET-AAS	[64]
PSTH Dowex$^{®}$ 1-X8	Pt	2 mol.l^{-1} HNO$_3$	ICP-OES	[65]
Bio-RadAG®MP-1M Bio-Rad AG® 1-X8 Bio-Rad AG® 1-X2	Pt, Rh	0,1 mol.l^{-1} TU	ICP-OES	[66]
PSTH-cpg	Pt, Pd, Ir	0,03% TU v 3,2% HNO$_3$	ICP-MS	[67]

Dow XUS 43600.00 Lewatit M+ MP600 Purolite S985	Pt, Pd, Rh	1 mol.l^{-1} TU v 2 mol.l^{-1} HCl	ICP-OES	[68]
Rossion-1p Rossion-5 Rossion-10	Pt, Pd, Rh, Ru, Ir	-	ICP-OES	[69]
Dowex® 50W-X8	Pt, Pd	0,5 mol.l^{-1} HCl	ICP-OES	[70]*
Dowex®1-X8(50-100) Dowex®1-X8(200-400) Dowex®1-X10(50-100)	Pt, Pd	0,5 mol.l^{-1} HCl 1 mol.l^{-1} HCl	ET-AAS	[71]*
Kationtoměniče				
Dowex® 50W-X8 Dowex® 50W-X12	Pt, Pd	-	ET-AAS	[71]*
Bio-Rad AG® 50W-X8	Ru, Rh, Pd,Ir, Pt	0,5 mol.l^{-1} HCl	ICP-MS	[72]
Dowex® 50W-X8	Pt, Pd, Rh	0,6 mol.l^{-1} HCl	ICP-MS	[73], [74]
Speciální sorbenty				
Separcol CARB Lignit C	Pt, Pd, Os Os, Ru	rozklad O_2 plazma	ICP-OES	[45]*
MWCNTs	Pd	0,4 mol.l^{-1} TU	FAAS	[75]
PEI/Al_2O_3	Pd	1 mol.l^{-1} TU v 1 mol.l^{-1} HCl	ET-AAS	[76]
CNF-PEI	Pt	-	ICP-OES	[77]

*Citace a práce pod vedením autorky

3.2 PŘÍNOS – VÝVOJ A INOVACE NOVÝCH SORPČNÍCH TECHNIK

Z **Tabulky 1**, která je aktuálním přehledem sorpčních technik, je patrné, že bylo poměrně významně přispěno k vývoji a inovaci sorpčních technik platinových kovů metodou SPE za použití různých typů sorbentů s využitím celé řady modifikačních činidel pro zvýšení selektivity celého procesu. Nejdůležitějšími parametry při testování každého sorpčního procesu bylo vždy množství sorbentu, účinnost sorpce a účinnost eluce, optimální rychlost sorpce, aplikace pro analýzu reálných vzorků (vody, kyselinové výluhy z půd, prachu, filtrů, biologického matriálu), spotřeba chemikálií a vznik chemického odpadu, dostupnost a cena sorbentu a v neposlední řadě kompatibilita chemického složení eluátu s analytickou koncovkou. Jako detekční techniky bylo využito metod atomové absorpční a atomové emisní spektrometrie. Dalšími možnými analytickými technikami pro stanovení platinových kovů jsou elektrochemické metody (voltametrie) nebo také chromatografické a elektromigrační metody, jejichž podrobný přehled z hlediska analýzy platinových kovů je přehledně publikován v práci [78], viz **Příloha 2**. Platinové kovy mohou být separovány ve formě komplexů s monodentálními ligandy (halogenokomplexy, thiokyanatokomplexy, kyanokomplexy, komplexy s thiomočovinou), iontových asociátů nebo chelátů (reakce s heterocyklickými azobarvivy, dithiokarbámaty, 8-hydroxychinolinem atd.) metodou kapalinové chromatografie (HPLC) nebo kapilární zónové elektroforézy (CZE). Výborných výsledků je např. dosaženo při separaci iontových asociátů halogenokomplexů platinových kovů s organickými amoniovými solemi metodou iontové chromatografie. Metody HPLC a CZE jsou používány zejména při přípravě a separaci sloučenin platinových kovů jako protirakovinných léčiv nebo testování metabolických produktů po léčbě onkologických pacientů.

V předkládaných publikacích (viz Přílohy) byla studována jak sorpce na modifikovaných silikagelech, tak na polymerních sorbentech typu kopolymeru styrenu a divinylbenzenu v kombinaci s celou řadou činidel a také na iontoměničích.

První velkou skupinu sorbentů tvoří modifikovaný silikagel. Samotný silikagel jako takový není příliš vhodný pro sorpci platinových kovů. Ty se v roztocích nacházejí nejčastěji ve formě halogenokomplexů (chlorokomplexů, méně pak bromokomplexů), v závislosti na použité metodě rozkladu a mineralizaci vzorku. Chlorokomplexy všech platinových kovů jsou poměrně stabilní a platinové kovy tak lze udržet v roztoku i ve velmi nízkých koncentrací, nejlépe v prostředí 0,1 mol.l^{-1} HCl. Při nižší kyselosti (vyšším pH) je nebezpečí sorpce platinových kovů na stěny nádob. Může tak docházet ke ztrátám analytu, což je limitující zejména při aplikačních analýzách reálných vzorků, ale také ke kontaminaci laboratorních pomůcek zpětným uvolňováním platinových kovů do roztoku (např. při optimalizaci sorpčního procesu, který je prováděn s vyššími koncentracemi platinových kovů).

Silikagel lze tedy výhodně modifikovat různými organickými funkčními skupinami. Nejčastěji to je oktadecyl, oktyl, kyanoethyl, fenyl a aminopropyl. Na takto vzniklý hydrofobní sorbent lze imobilizovat vhodná komplexační nebo chelatační činidla. Při vývoji nových sorpčních technik byly s výhodou použity kvartérní amoniové soli. Nejvýznamnější se ukázaly být kationaktivní tenzidy s vysokomolekulárním hydrofobním kationtem, což jsou silné báze dobře rozpustné ve vodě a plně disociované v celém rozsahu pH. V přítomnosti halogenokomplexů platinových kovů pak vznikají stabilní iontové asociáty, které jsou z vodného prostředí dobře sorbovány na modifikovaný silikagel, nejčastěji silikagel C18. Interakce těchto iontových asociátů se sorbentem má však komplikovanější charakter a sorpce probíhá několika mechanismy. Asociačním reakcím významně napomáhá symetrie tenzidů s dlouhým alkylovým řetězcem a výrazným hydrofobním charakterem. Hydrofilní ion je obklopen hydrofobními alkylovými řetězci, které mají významnou afinitu k použitému sorbentu. Adsorpční schopnost, a tedy i účinnost sorpce, narůstá v závislosti na délce alkylového řetězce. K desorpci jsou využívána organická rozpouštědla mísitelná s vodou, která snižují stupeň pokrytí sorbentu nasorbovaným iontovým asociátem.

Obecně jsou jako iontové asociáty (iontové páry) označovány částice, vznikající vlivem přitažlivých elektrostatických sil mezi opačně nabitými ionty. Asociáty lze také považovat za meziprodukty interakce mezi těmito opačně nabitými ionty, která často vede až ke vzniku komplexních sloučenin. Podle souvislosti mezi konstantou stability vzniklého asociátu a relativní permitivitou rozpouštědla (vody) je asociace tím větší, čím je menší dielektrická konstanta prostředí a vzdálenost mezi ionty. Vzniklé elektroneutrální částice se velice snadno extrahují do nepolární fáze, ať už pevné nebo kapalné, čehož lze výhodně využít pro jejich zakoncentrování. Extrahovatelnost pak závisí na velikosti iontů, jejich náboji a na délce alkylového řetězce, popř. jeho rozvětvení. Iontový pár se bude extrahovat tím snadněji, čím jeho náboj nižší a rozměr větší.

Pilotní prací, využívající sorpci iontových asociátů na silikagelu C18, byla práce z roku 1999 [50], **Příloha 3**. V této práci je pro prekoncentraci všech platinových kovů jako asociační činidlo využit kationtový tenzid Septonex®, (α-carbethoxypentadecyl) trimethylammonium bromid. Tato rozsáhlá práce, jež byla mojí diplomovou prací, vypracovanou při magisterském studiu oboru Analytická chemie, na Přírodovědecké fakultě Masarykovy univerzity v Brně, obsahuje jak optimalizaci nově vyvinuté prekoncentrační techniky ve spojení s metodami ICP-OES a ICP-MS, tak její ověření za použití certifikovaného referenčního materiálu pevných výfukových zplodin, ale i praktickou aplikaci při analýzách reálných vzorků polétavého prachu, zachyceného na filtrech v pěti meteorologických stanicích ČHMÚ v ČR. Podrobnosti k aplikačním analýzám jsou uvedeny v kapitole **Přínos – aplikace a využití nových sorpčních technik při studiu kontaminace životního prostředí**. Tato práce má do dnešní doby poměrně mnoho citačních ohlasů a posloužila jako základ pro další vývoj sorpčních technik platinových kovů v celosvětovém měřítku.

Podrobněji a také s rozsáhlejšími praktickými aplikacemi byla tato prekoncentrační technika rozpracována a publikována v publikaci [51], **Příloha 4**. V této práci byly testovány sorpce chlorokomoplexů a bromokomplexů všech platinových kovů a také zlata na různé varianty modifikovaných sorbentů za použití tvorby iontových asociátů s různými kationaktivními tenzidy ve spojení s technikou ICP-OES. Jako sorbenty byly použity materiály od různých výrobců, silikagel modifikovaný okadecylem, oktylem, kyanoethylem, fenylem, aminopropylem a také čistý silikagel. Dalšími sorbenty pak byly makroporézní kopolymer styrenu a divinylbenzenu, Amberlity typu XAD2 a XAD4 a aniontoměničový sorbent na bázi silikagelu. Všechny o velikosti částic 63-100 μm. Z kationaktivních tenzidů byl testován Septonex® (α-carbethoxypentadecyl trimethyl ammonium bromid), Sterinol® (benzyldodecyldimethyl ammonium bromid), Ajatin® (benzyldimethyldodecyl ammonium bromid), trimethyl(tetradecyl) ammonium bromid, hexadecyl(trimethyl) ammonium chlorid a 1-hexadecylpyridinium chlorid. Byly optimalizovány podmínky sorpce z hlediska vhodné průtokové rychlosti, koncentrace kationaktivního tenzidu, volby optimálního elučního činidla, sorpční účinnosti jednotlivých sorbentů, vlivu objemu sorbovaného roztoku a množství sorbovaných platinových kovů a zlata a vliv interferentů, doprovodných kationtů a také vliv huminových kyselin. Za optimálních podmínek docházelo k 100% účinnosti simultánní sorpce na modifikovaný silikagel a eluce acetonitrilem pro platinu, palladium a zlato. Při použití aniontoměniče byly se 100% účinností zadrženy chlorokomplexy platiny, palladia a iridia s účinnou elucí 5 mol.l^{-1} HCl nebo HNO_3. Optimalizované postupy byly ověřeny při analýzách vzorků půd, elektrárenského popílku a přírodních vod, do kterých bylo přidáno známé množství platinových kovů a zlata, a byla tak ověřena účinnost sorpce a vliv matrice reálných vzorků.

Publikace [23], **Příloha 5**, studuje aplikaci prekoncentrační techniky pro stanovení platiny sorpcí iontového asociátu s kationaktivním tenzidem na silikagelu modifikovaného oktadecylovým řetězcem, nově ve spojení se stanovením metodou ET-AAS, která poskytuje pro platinu nižší hodnotu LOD. Po optimalizaci podmínek měření Pt na ET-AAS byly optimalizovány sorpční a eluční podmínky, vliv acidity sorbovaného roztoku a poměrně rozsáhlé studium vlivu doprovodných kationtů a aniontů v různém nadbytku oproti sorbovanému množství platiny. Účinnost sorpčního a elučního procesu byla pro platinu 96 %. Tento optimalizovaný postup sorpce a detekce byl aplikován při podrobném studiu obsahu platiny v polétavém prachu na území města Brna, ČR. Metodika byla také využita při monitoringu kontaminace silničního prachu, půd a vegetace v okolí komunikací [25], **Příloha 6**. Validace celého postupu analýzy – tedy rozkladu vzorku v *aqua regia*, sorpčního a elučního procesu s následným stanovením ET-AAS proběhla za použití certifikovaného referenčního materiálu tunelového prachu se známým obsahem platiny (BCR® 723). V současné době není k dispozici žádný jiný certifikovaný referenční environmentální materiál pro platinové kovy. Výsledky analýz environmentálních vzorků jsou podrobněji komentovány v kapitole **Přínos – aplikace a využití nových sorpčních technik při studiu kontaminace životního prostředí**.

Tato metodika předúpravy, prekoncentrace a stanovení platiny byla optimalizována i pro stanovení palladia [28], **Příloha 7,** tak, aby mohla sorpce i eluce Pt a Pd probíhat v jednom kroku za stejných experimentálních podmínek. Jako eluční činidlo byl využit acetonitril a bylo dosaženo 100% účinnosti sorpce jak pro platinu, tak pro palladium. Tato metodika byla využita pro stanovení Pt a Pd v biologických vzorcích ze znečištěných oblastí města Brna. Podrobnosti k environmentálním analýzám jsou uvedeny v kapitole **Přínos – aplikace a využití nových sorpčních technik při studiu kontaminace životního prostředí**.

V **Příloze 8** je uvedena publikace [48] studující novou inovativní prekoncentrační techniku na polymerním sorbentu pro simultánní stanovení platinových kovů metodou ICP-MS. Pro sorpci platinových kovů byla využita tvorba a vznik chelátu analytu s vhodnými organickými chelatačními činidly. Selektivní sorpce platinových kovů byla zajištěna přítomností heteroatomu v molekule organického činidla. Jako sorbent byl použit polymerní sorbent kopolymeru styrenu a divinylbenzenu a jako chelatační činidla byly testovány ammonium-pyrolidindithiokarbamát, thiomočovina, 4-(2-pyridylazo) resorcinol a 8-hydroxychinolin-5-sulfonová kyselina. Sorbent byl před sorpcí takto vzniklých chelátů kondicionován kationaktivním tenzidem. Testovány byly Zephyramin® (benzyldimethyltetradecyl ammonium chlorid), Septonex® (α-carbethoxypentadecyl trimethyl ammonium bromid) a Ajatin® (benzyldimethyldodecyl ammonium bromid). Byla testována a optimalizována účinnost sorpčního a elučního procesu, vliv acidity prostředí a také vliv interferenčních iontů v 10^4 nadbytku oproti sorbovanému množství platinových kovů. Nejúčinnější sorpční postup sestával z kondicionace sorbentu Strata SDB-L roztokem Septonexu® v 0,1 $mol.l^{-1}$ HCl, sorpce platinových kovů z roztoku obsahujícího 1.10^{-5} $mol.l^{-1}$ PAR s následnou elucí 10 ml směsi acetonitrilu a 0,1 $mol.l^{-1}$ HCl v poměru 4:1. Za těchto podmínek byla dosažena 100% návratnost sorpce pro platinu, palladium a osmium. Sorpční účinnost pro ruthenium a iridium byla pouze 40 % a u rhodia nedošlo tímto sorpčním postupem k zachycení na sorbentu. Optimalizovaný postup sorpce byl ověřen na reálných vzorcích přírodních vod a lišejníků se známým přídavkem platinových kovů a nebyl zjištěn žádný matricový efekt na účinnost prekoncentrace i samotného stanovení technikou ICP-MS.

Jak již bylo řečeno v úvodu, na některé sorbenty lze s výhodou navázat funkční skupiny nebo činidla, která významně ovlivní selektivitu následné sorpce. Dioximy jsou považovány za činidla s nejvyšší selektivitou a jsou známy a používány v analytické chemii již od minulého století. Diacetyldioxim je vysoce selektivním činidlem právě pro palladium (II), které s ním jako jediné ze skupiny platinových kovů reaguje. Vzniklé komplexy zaujímají čtvercově planární strukturu, kde dva ligandy jsou spojeny vodíkovou vazbou, tvořící komplex v poměru kov:ligand 1:2, který je pak účinně zachycen na silikagelu modifikovaném C18. Nejnovější práce [60], **Příloha 9**, publikuje originální výsledky nového sorpčního selektivního postupu pro stanovení palladia s využitím specifického chelatačního činidla diacetyldioxim. Tento způsob zachycení ultrastopových koncentrací palladia byl inspirován prací [53]. Při pokusech za experimentálních podmínek uvedených v této práci nebylo ale dosaženo uspokojivých výsledků. Sorpce palladia neprobíhala kvantitativně, pouze ze 40 %. Volbou vhodnějšího sorbentu, eluentu i dalších parametrů a podmínek sorpce byla v práci [60] tato metodika inovována a dosaženo 100% návratností pro palladium. Aby se zajistila tvorba komplexu palladia a diacetyldioximu, $Pd(DMG)_2$, musí být vždy přítomno selektivní činidlo v nadbytku ve srovnání s Pd. V této práci bylo zjištěno, že nejlepších výsledků sorpce bylo dosaženo, když byl komplex $Pd(DMG)_2$ již vytvořen v roztoku před tím, než byl adsorbován na sorbent ovlhčený redestilovanou vodou. Naopak, když byl sorbent pouze kondicionován pomocí DMG a byl sorbován pouze roztok Pd, sorpce nebyla kvantitativní. To mohlo být způsobeno nedostatečným množstvím sorbovaného činidla nebo průtokem, který byl během sorpce příliš vysoký. Nejúčinnějším elučním činidlem pro nasorbovaný komplex $Pd(DMG)_2$ byla 1 mol.l^{-1} HCl v absolutním etanolu. Palladium bylo po prekoncentračním procesu stanoveno metodu HR-CS-GF-AAS, tedy atomovou absorpční spektrometrií s grafitovou kyvetou, kontinuálním zdrojem záření a monochromátorem o vysokém rozlišení.

Pro srovnání sorpce komplexu $Pd(DMG)_2$ byla provedena také sorpce palladia na komerčně dostupném sorbentu Quadrasil® TA s vysokou afinitou k platinovým kovům. Sorbent Quadrasil® je registrován ochrannou známkou firmy Johnson & Matthey. Jedná se o řadu selektivních a specifických sorbentů, připravovaných funkcionalizací oxidu křemičitého. Navázáním vybraných funkčních skupin nebo řetězců se dosáhne vysoké selektivity sorpce pro vybrané kovové ionty. Tyto sorbenty jsou velmi robustní, využitelné v široké koncentrační škále, mechanicky, tepelně a chemicky odolné, s malou tendencí k botnání. Lze je využít jak pro sorpce z vodných, tak i organických roztoků v celé škále pH. Jako funkční skupina, která zajišťuje vysokou afinitu k vybraným iontům kovů, bývá použit aminopropyl (AP), merkaptopropyl (MP), sulfonová kyselina (SA), aminoimidazol (IMDAZ), fenolimin (PHI) a také triamin (TA). Ten má významnou sorpční schopnost iontů platiny, palladia a rhodia v důsledku významné afinity sloučenin platinových kovů k organickým sloučeninám, obsahujícím heteroatom dusíku. Inspirací k výběru tohoto sorbentu publikace [79]. Po úpravě sorpčních parametrů při optimalizaci za našich podmínek (zejména použité množství sorbentu) bylo pro palladium dosaženo 99% návratnosti při použití 0,05 mol.l^{-1} thiomočoviny jako eluentu.

Pro zhodnocení obou sorpčních postupů (Pd jako komplex s DMG a sorpce na komerčně dostupném sorbentu Quadrasil® TA) z hlediska jejich použitelnosti pro analýzu reálných vzorků z životního prostředí byl podrobně studován vliv doprovodných iontů. Výrazně negativní vliv na účinnost sorpce byl zaznamenán pro sorbent Quadrasil® TA již v přítomnosti 100-násobného množství všech testovaných iontů, což se u sorpce komplexu $Pd(DMG)_2$ na silikagel C18 neprojevilo. Pro reálné aplikace při studiu kontaminace životního prostředí palladiem byla tedy zvolena sorpční metoda s činidlem DMG. Podrobnosti k analýze kontaminace životního prostředí jsou uvedeny v kapitole **Přínos – aplikace a využití nových sorpčních technik při studiu kontaminace životního prostředí**.

Velkou skupinou sorbentů používaných pro separaci i prekoncentraci platinových kovů jsou iontoměniče, zejména pak aniontoměniče, kde jsou aniontové komplexy platinových kovů účinně zachycovány, popř. kationtoměniče, kde nedojde k zadržení komplexů platinových kovů, ale dojde k jejich separaci od částí matrice, které by mohly rušit jejich stanovení. Nízkokapacitní aniontoměniče silně poutají inertní aniontové halogenokomplexy platinových kovů a jejich eluce ze sorbentů je poměrně obtížná. Jako eluční činidla bývají nejčastěji využívány roztoky silných minerálních kyselin nebo solí, např. $NaClO_4$. Tento separační postup také zaručuje oddělení všech kationtů kovů od platinových kovů, které se ve svých roztocích nacházejí ve formě aniontových komplexů. Zvýšená koncentrace kyselin a solí v eluátu však může působit rušivě při koncovém analytickém stanovení. Jak je z **Tabulky 1** patrné, byla testována také celá řada iontoměničů, zejména v diplomových pracích [70-71] a v disertační práci [45]. Výhodou je jejich nízká cena a dostupnost, nevýhodou pak nízká selektivita a problémy při detekci stopových koncentrací platinových kovů v silně zasolených roztocích. Za optimalizovaných podmínek dosáhly návratnosti sorpcí 100 % pro platinu i palladium a tyto postupy byly aplikovány při analýzách půd v okolí frekventovaných silnic, viz kapitola **Přínos – aplikace a využití nových sorpčních technik při studiu kontaminace životního prostředí**.

Jak již bylo uvedeno výše, problematika platinových kovů je posledních 30 let neustále aktuální. První prací, kterou jsem v problematice platinových kovů publikovala v roce 1999, byl přehled prekoncentračních SPE metod *„Solid phase extraction and preconcentration for the determination of trace amounts of platinum group metals in environmental and biotic material - A critical review“* [43], **Příloha 1**. Mojí zatím poslední prací, přijatou do tisku (10/2019) v prestižním odborném časopise z oblasti analytické chemie *Trends in analytical chemistry*, je také review [80], **Příloha 10**, s názvem *„Recent advances in the preconcentration and determination of platinum group metals in environmental and biological samples“*. Je zde přehledně shrnut vývoj nových prekoncentračních postupů a trendů v této oblasti právě za posledních 20 let.

Aktuálnost problematiky platinových kovů potvrzují neustále nové přístupy a vývoj nových metod separace, prekoncentrace a stanovení a jejich aplikace při analýzách reálných environmentálních a biologických vzorků, publikované v odborných mezinárodních publikacích.

4 PLATINOVÉ KOVY V ŽIVOTNÍM PROSTŘEDÍ

4.1 SOUČASNÝ STAV VÝSKYTU PLATINOVÝCH KOVŮ V ŽIVOTNÍM PROSTŘEDÍ

Ve srovnání s ostatním prvky se platinové kovy přirozeně nacházejí v životním prostředí ve velmi nízkých koncentracích, často v elementární formě a jejich výskyt má difuzní charakter. Všechny platinové kovy se vyskytují vždy společně. Palladium a platina jsou zastoupeny nejvíce, v obsahu 0,015-0,010 mg.kg^{-1}, Ru, Os, Rh a Ir pak v koncentracích o řád nižších 0,005-0,0001 mg.kg^{-1}. Přirozeně se vyskytují buď v ryzí formě rozptýleny v aluviálních rýžovištích, nebo vázány v rudách jako arsenidy a sulfidy spolu s ostatními běžnějšími kovy, jako jsou nikl, měď a železo [1], [36]. Největší naleziště se nacházejí na jihu Afriky, v Rusku a Severní Americe.

I když jsou tyto kovy přirozeně vzácné, od konce 20. století jejich obsah v životním prostředí vlivem antropogenní činnosti člověka neustále narůstá. Důsledkem je jejich masivní používání v dopravě, průmyslu a v lékařství. To jsou hlavní cesty vstupu těchto kovů a jejich sloučenin do složek životního prostředí.

Platinové kovy jsou používány především pro své excelentní katalytické vlastnosti a nachází uplatnění v průmyslu především právě jako katalyzátory. Palladium se používá při hydrogenačních a dehydrogenačních reakcích, platina jako katalyzátor při výrobě kyseliny dusičné, reformování ropy a zejména pak oba tyto kovy v automobilových katalyzátorech. Ostatní platinové kovy se používají pro zvýšení tvrdosti různých slitin a při katalytických a hydrogenačních reakcích. Jejich větší průmyslové využití je však omezeno jejich vzácností a vysokou cenou. V posledních letech vzrostlo použití palladia, které částečně nahradilo platinu v automobilových katalyzátorech. Důvodem byla jeho snadnější dostupnost a nižší cena, která ovšem jeho zvýšeným využíváním vzrostla.

Katalyzátory na bázi platiny se při výrobě kyseliny dusičné používají již zhruba sto let. Moderní postupy výroby kyseliny dusičné sestávají ze třech kroků. Prvním krokem je oxidace plynného amoniaku vzduchem za vzniku oxidu dusnatého, pro dosažení vysoké účinnosti přeměny za tlaku na platinovo-rhodiovém katalyzátoru. Rhodium je přidáváno pro snížení ztrát platiny. Oxid dusnatý se ochladí a dále se oxiduje na oxid dusičitý, který se pak absorbuje ve vodě na kyselinu dusičnou. Ztráty platiny a rhodia mohou dosahovat až 300 mg na 1 t kyseliny dusičné. Konečné použití kyseliny dusičné je při výrobě dusíkatých hnojiv, důležitého zdroje rostlinných živin. Touto cestou platina také významně vstupuje do životního prostředí. Ztráty platiny na katalyzátorech činí celosvětově několik tun ročně.

Pro použití platinových kovů v automobilovém průmyslu bylo celosvětově v roce 2018 využito cca 95 t platiny, palladia ovšem již 270 t a rhodia pouze cca 27 t. S postupem doby se stále více vzácných kovů recykluje. V roce 2018 bylo z použitých autokatalyzátorů recyklováno téměř 65 t platiny, 100 t palladia a cca 11 t rhodia. Recyklované automobilové katalyzátory mohou obsahovat až 2000 g.t^{-1} platiny, což je významně vyšší obsah než v rudách, ze kterých je těžena. Tyto vysoké koncentrace platiny v odpadu jej činí ekonomicky velmi zajímavým, ve srovnání s ekonomickou stránkou získávání platiny těžbou z rud.

Silniční doprava je jednoznačně největším zdrojem znečištění prostředí platinovými kovy. Existují studie, které předpokládají až 40% uvolnění platinových kovů z katalyzátorů do životního prostředí během prvních najetých 100 000 km automobilu [81]. Emise PTK byly prokázány jak zkušebními testy emisních plynů v laboratořích, tak stanovením jejich přítomnosti ve složkách životního prostředí. Toto uvolňování během provozu katalyzátoru je způsobeno chemickými a fyzikálními procesy, které probíhají na katalytickém povrchu. Dochází k uvolňování vlivem mechanické abraze, vysokou provozní teplotou a probíhajícími oxidačně-redukčními reakcemi. Uvolňování je dále ovlivněno řadou faktorů, jako je rychlost a styl jízdy, jízda stylem start-stop, druh a kvalita paliva, stáří katalyzátoru a zejména pak druh motoru. Výrazně vyšší emise má dieselový motor než motor benzínový s třícestným katalyzátorem. V závislosti na těchto uvedených faktorech mohou emise dosahovat množství v rozsahu ng až μg PTK na 1 km jízdy, což následně představuje jejich obsahy v kontaminovaném vzduchu v okolí frekventovaných silnic a křižovatek v $\mathrm{pg.m^{-3}}$ [23]. Přesné množství uvolněné platiny však nelze, s ohledem na množství faktorů ovlivňujících jejich uvolňování, zjistit nebo předpovídat.

Emitované PTK jsou nejčastěji ve formě kovových nanočástic (viz kapitola **Nanočástice platiny**), které mohou být adsorbovány na částečky nosiče katalyzátoru (Al_2O_3) nebo výfukových zplodin (saze). Částice se po uvolnění stávají součástí znečištěné atmosféry a dle velikosti se pak deponují v různé vzdálenosti od zdroje znečištění v závislosti na hustotě automobilové dopravy, meteorologických podmínkách a morfologii terénu. Ulpívají v okolí silnic na prachu, v povrchových vrstvách půdy a na vegetaci a za jistých podmínek mohou podlehnout i dálkovému transportu. Důkazem toho je nalezení zvýšené koncentrace PTK ve sněhu a ledu v evropských horských oblastech i v Grónsku, s významným nárůstem od 90. let minulého století [81]. Výhodou analýzy různých vrstev ledu jsou zejména chronologické informace, které mohou indikovat časové období kontaminace.

Dalším významným zdrojem PTK je lékařství. Léky na bázi platiny, zejména cisplatina, cis-diaminodichloro Pt(II), karboplatina a cis-(diamin-1,1-cyklobutan-1,1-dikarboxylato) Pt(II), jsou široce používány jako účinná cytostatika již od 70. let minulého století. Principem protinádorového působení cisplatiny je inhibice syntézy DNA vytvořením příčných vazeb v řetězci a mezi řetězci DNA. Cytotoxický účinek cisplatiny je způsobený vazbou na všechny báze DNA, s preferencí pozic guaninu a adenosinu. Kromě inhibice syntézy DNA má cisplatina imunosupresivní, radiosenzibilizující a antibakteriální vlastnosti. Používá se k léčbě široké škály karcinomů – bronchogenního karcinomu, testikulárního karcinomu, ovariálního karcinomu, karcinomu cervixu, endometria, prostaty, močového měchýře, melanomu, sarkomů, nádorů ORL, karcinomu mozkového epitelu a maligních lymfomů [82]. Oproti terapeutickým účinkům má však cisplatina celou řadu negativním účinků na léčeného pacienta. Při použití působí nefrotoxicky (poškození ledvin), neuropaticky (poruchy periferních nervů), ototoxicky (ohrožení sluchového ústrojí), vyskytují se alergické projevy, zhoršuje se jaterní funkce a krevní obraz, je podezřelá z možné karcinogenity (vznik akutní leukemie) a má mnoho dalších nežádoucích vedlejších účinků. Vylučování cisplatiny, i ostatních platinových metalofarmak, probíhá výhradně močí a žlučí. V prvních pěti dnech se vyloučí z těla pacienta 27-43 % podané látky. Takto se platina dostává do odpadních vod nejen léčebných zařízení, ale i domácností po odchodu pacientů domů. Její koncentrace v odpadních vodách se pohybují řádově v $ng.l^{-1}$.

Hlavním problémem výskytu platinových léčiv v odpadních vodách je přítomnost platiny v rozpustné, biodostupné a značně toxické formě, na rozdíl od inertnějších kovových forem platiny, emitovaných automobilovými katalyzátory. Tyto však mohou být částečně ve formě povrchově oxidovaných částic, které pak snadněji podléhají zejména komplexačním reakcím a vznikají biologicky dostupné formy platiny, nejčastěji v podobě chlorokomplexů nebo komplexů s organickými ligandy. Nejčastějšími ligandy, komplexujícími platinu, jsou fosfáty (z fosfátových hnojiv), chloridy (z povrchové údržby vozovek v zimních měsících), citráty (produkované kořeny rostlin) a fulvové kyseliny (vznikající přirozeným rozkladem organické hmoty) [83]. Doposud existuje jen velmi málo relevantních informací o biologické dostupnosti platinových kovů, jejich ekotoxicitě a osudu v životním prostředí.

Důležitým parametrem při hodnocení chování platinových kovů ve složkách životního prostředí je jejich mobilita. Ta jednoznačně závisí na formě PTK, v půdách pak na pH, redoxním potenciálu a přítomností výše uvedených komplexačních činidel [83]. Existují předpoklady, že okolo 10 % platiny emitované z autokatalyzátorů je za environmentálních podmínek rozpustné ve vodě, pro palladium a rhodium se předpokládá rozpustnost dokonce až 50 % [10]. S tím je spojena jejich prokázaná vyšší biodostupnost. Ta byla experimentálně zjištěna v pořadí $Pd > Pt \geq Rh$, testováním transformačního koeficientu (poměr koncentrací kovu v rostlině a v půdě, ze které rostlina vyrůstá). Palladium je tedy ze všech platinových kovů nejvíce rozpustné, mobilní a biodostupné. Jeho nejvyšší koncentrace byly zjištěny v kořenech rostlin, kde se předpokládá vazba na látky s obsahem síry, v tělních tekutinách živočichů a v peří ptáků [84].

V transportu platinových kovů v tělech živočichů mají rozhodující roli krevní proteiny, až 80 % platiny v krvi bylo nalezeno v erytrocytech. Stabilita vazby na protein závisí na druhu sloučeniny. Zvýšené koncentrace byly detekovány v ledvinách a játrech, kde se platinové kovy váží na metalothioneniny (proteiny bohaté na cystein). Ty mají vysokou afinitu ke všem těžkým kovům (např. Cd, Cu, Hg atd.) a tvorba metalothioneinů indikuje obecně přítomnost těchto rizikových prvků. Pt(II) tvoří vazbu s těmito proteiny až 100-krát rychleji než ostatní těžké kovy, může tak dojít i k jejich vytěsnění. Relevantní informace o chování ostatních platinových kovů a jejich sloučenin nejsou doposud známy. Stejně tak nejsou známy informace o biotransformačních reakcích platinových kovů tvorbou methylových sloučenin. Byly provedeny pouze laboratorní studie a neexistují přímé důkazy o methylaci platinových kovů za environmentálních podmínek.

Toxicita PTK v životním prostředí závisí jednoznačně na jejich velikosti (u emitovaných částic), oxidačním stavu a sloučeninách, ve kterých se vyskytují. V elementární kovové formě jsou inertní, avšak v podobě nanočástic, vlivem rozpouštění, oxidačních a komplexujících reakcí, jak za biotických, tak abiotických podmínek, dochází ke zvýšení jejich toxicity. Z materiálů Světové zdravotnické organizace (WHO) [13-14], poskytující data pouze pro platinu a palladium, vyplývá nebezpečí při vdechnutí pevných částic a dále jejich alergizující vlastnosti. Pd (II) je dokonce nejčastější senzibilizátor ze všech kovů. Největší riziko spočívá především v chronické expozici obyvatel žijících ve znečištěných oblastech. V současnosti byly nalezeny ve velkých městských aglomeracích zvýšené obsahy platinových kovů ve všech složkách životního prostředí. Jejich množství neustále narůstá a jednoznačně závisí na hustotě automobilové dopravy. Obyvatelé těchto oblastí jsou tedy nejvíce ohroženou skupinou obyvatelstva [12], [25], [28], [81] a [84].

Analýza jednotlivých složek životního prostředí může probíhat několika způsoby. Při analýze znečištěné atmosféry se odebírají automatickým vzorkovačem pomocí prosávání znečištěného vzduchu vzorky pevných částic polétavého prachu zachycením na filtrech ze skleněných vláken. Ty se pak dále analyzují a z objemu prosátého vzduchu při vzorkování lze určit koncentraci analytu v atmosféře, u platinových kovů nejčastěji v jednotkách pg.m^{-3}. Použitím 24 hodinového vzorkování lze dosáhnout zakoncentrování analytu na filtru. Při interpretaci výsledků a vyvozování závěrů je nutno zohlednit podmínky při odběru vzorku (roční období, doba odběru – pracovní dny, víkendy, intenzita dopravy, meteorologické podmínky atd.).

Nejsnadněji analyzovanou matricí je voda a vodné roztoky. Nevýhodou při analýze vzorků vody z životního prostředí jsou velmi nízké obsahy platinových kovů, které se pohybují v jednotkách ng.l^{-1}. V tomto případě je nezbytné použít některé prekoncentrační techniky pro nabohacení analytu na měřitelnou hodnotu koncentrací. Lze tak zvýšit obsah analytu v analyzovaném vzorku i o jeden řád, s ohledem na použitou koncovou detekční instrumentální analytickou techniku.

Velice úzce s analýzou přírodních vod souvisí analýza sedimentů. Pro komplexní přehled o chování platinových kovů ve vodách je zajímavým analytem sediment, odebraný ve stejném místě jako vzorek vody. Při odběru vzorku sedimentu však mohou nastat komplikace a ztráty analytu. Při hodnocení obsahu platinových kovů v sedimentech je nutno zohlednit možnou nehomogenitu vzorků sedimentu a vliv místních podmínek (přítomnost jiných znečišťujících látek, chování toku v místě odběru, klimatické podmínky atd.).

Velmi často analyzovaným materiálem je půda v okolí frekventovaných silnic. Při odběru půdy je třeba dbát na řadu faktorů: vzdálenost místa vzorkovaní od potenciálního zdroje kontaminace (od komunikace), na hloubku, ze které je vzorek odebírán, na intenzitu dopravy v daném místě, místní podmínky (přítomnost vegetace, terénních bariér atd.), klimatické a meteorologické podmínky.

Silniční prach je také důležitou matricí pro hodnocení stavu znečištění prostředí z automobilové dopravy. Jeho odběr je náročnější a musí být dodrženy bezpečnostní předpisy při jeho odběru, zejména pak pokud se jedná o odběr vzorků tunelového prachu. V této matrici se předpokládá nejvyšší obsah platinových kovů a potvrzují to i data v **Tabulce 2**.

Pro komplexní přehled o distribuci platinových kovů ve složkách životního prostředí je nezbytné stanovit jejich obsah také v biologických matricích, v tzv. bioindikátorech.

K tomuto účelu slouží účinný nástroj – biomonitoring. Pomocí biomonitoringu lze najít vztahy mezi znečištěním jednotlivých složek životního prostředí (ovzduší, vodního a terestrického ekosystému) a organismy v něm žijícími. Z dat získaných biomonitoringem lze také predikovat možné nežádoucí vlivy na lidské zdraví [85]. Bioindikátorem je organismus, pomocí něhož se indikuje zatížení životního prostředí vybranými polutanty. Nejčastěji se používají rostlinné bioindikátory a dělí se na senzitivní, akumulační a testovací. V případě biomonitoringu platinových kovů se využívají akumulační bioindikátory se schopností akumulace polutantů ze složek životního prostředí. Tyto látky se v organismu hromadí, aniž by způsobily jeho viditelné poškození, a jejich příjem závisí na koncentraci v prostředí. Tyto bioindikátory se dají analyzovat ihned po odběru - pasivní bioindikace, nebo využitím aktivní (expoziční) bioindikace. Vybrané druhy rostlin jsou záměrně vystaveny vlivům znečištěného prostředí a reagují akumulací polutantu (akumulační indikátor). Mezi snadno a celoročně dostupné bioindikátory patří mechy, lišejníky a jehličí. Tyto bioindikátory mají tu výhodu, že jsou stálezelené a lze je vzorkovat celý rok. Navíc mají mechy a lišejníky velký povrch těla, který není pokryt kutikulou. Tím je umožněn příjem polutantů z atmosféry téměř výhradně procesem depozicí částic. Dále bývají analyzovány vzorky travní vegetace, často zároveň s analýzou půdy ze stejného místa. I při vzorkování biologických vzorků je nutno zohlednit podmínky vzorkování – roční období, klimatické a meteorologické podmínky, druh odebíraného vzorku, vzdálenost od zdroje kontaminace atd.

Aktuální přehled výskytu platinových kovů ve složkách životního prostředí, s uvedením lokality a detekční analytické techniky je uveden v **Tabulce 2**.

Tabulka 2 Přehled výskytu platinových kovů v environmentálních a biologických vzorcích

Matrice	Lokalita	Analyt / konc.	Detekce	Literatura
Vzduch		(pg.m^{-3})		
	Brno, Česká republika	Pt 12-35 Pd 37-61	ICP-MS	[86]*
	Meteorologické stanice ČHMÚ, Česká republika	Pt 9-62 Pd <LOD-283	ICP-OES ICP-MS	[50]*
	Mnichov, Německo	Pt 62.00-21.50	-	[87]
	Brno, Česká republika	Pt 2.3-51.5	ET-AAS	[23]*
	Záhřeb, Chorvatsko	Pt 0.488-1.071 Pd 3.856-5.600 Rh 0.444-0.750	ICP-MS	[24]
Voda		**(pmol.l^{-1})**		
Dešťová voda	Záliv Tokyo, Záliv Otsuchi,	Pt 0.12-0.62 Pt 0.07-6.51	ICP-MS	[20]

Říční voda Mořská voda	Japonsko	Pt 0.29-7.74		
Vodovodní voda	Brno, Česká republika	(ng.l^{-1}) Pt < LOD (0.054)	AdSV	[88]*
Mořská voda	-	(fg.g^{-1}) Pt 0.1-100	-	[89]
Mořská voda	Atlantský oceán	Pt 0.11-0.32	AdCSV	[90]
Sediment		(ng.g^{-1})		
Mokřadní sediment	Perth, Austrálie Mokřadní sedimenty	Pt 9.0-103.8 Pd 5.4-61.2 Rh 1.5-17.2	ICP-MS	[74]
Říční sediment	Ústí řek Tagus a Prodelta, Portugalsko	Pt 9.5	AdCSV	[91]
	Ústí řeky Gironde, Francie	(pmol.g^{-1}) Pt 1.0-7.0	AdCSV	[92]
	Svratka, Brno, Česká republika	Pt 8.839-48.82 Pd 1.800-7.674 Rh <LOD	ET-AAS	[31]*
Estruární sediment	Středomořské pobřeží	Pt 6.0-15.0	DPV	[32]
Půda		(ng.g^{-1})		
	Palermo, Itálie	Pt 0.6-2210	AdCSV	[26]
	Brno, Česká republika	Pt 4.9-100.8	ET-AAS	[93]*
	Toronto, Kanada	Pt 59 Pd 98 Rh 9.6	ICP-MS	[94]
	Brno, Česká republika	Pt 20.5-186.1	ET-AAS	[71]*
	Berlín, Německo (1992-2013)	Pt 1.28-4.05 Pd 0.305-1.69 Rh 0.0450-0.330	ICP-MS	[27]
	Brno, Česká republika	Pt 10.5-15.7	ET-AAS	[25]*
Prach		(ng.g^{-1})		
Silniční prach	Brno, Česká republika	Pt 2.8-503 Pd 11-40	ICP-MS	[86]*
Polétavý prach	Brno, Česká republika	Pt 61.9-2997.7	ET-AAS	[23]*
Silniční prach	Toronto, Kanada	Pt 26-69 Pd 10-121	ICP-MS	[94]

		Rh 7.8-15		
Tunelový prach	Brno, Česká republika	Pt 66.3-192 Pt 29.2-38.2	ET-AAS	[25]*
Biologické vzorky		(ng.g^{-1})		
Kůra stromů	Městské oblasti Venkovské oblasti	Pt 12.9 Pt 5.5	ICP-MS	[8]
Lišejníky	Brno, Česká republika	Pt <LOD-23.18 Pd 5.140-47.08	ET-AAS	[28]*
Mechy		Pt <LOD-59.40 Pd 2.979-8.449		
Jehličí		Pt <LOD-7.278 Pd 3.017-12.09		
Lišejníky	Brno, Česká republika	Pd 5.8-23.6	HR-CS-GF-AAS	[60]*
Tráva	Brno, Česká republika	Pt 10.0-11.6	ET-AAS	[25]*
Ústřice	Ústí Gironde, Francie	(pmol.g^{-1}) 0.80-3.1	AdCSV	[92]
Škeble říční - lastura	Svratka, Brno, Česká republika	Pt 11,72-21,68 Pd 2,99-5,395	ET-AAS	[31]*
Mušle	Středomořské pobřeží	Pt 0.09-0.66	AdCSV	[32]
Tělní tekutiny		(ng.g^{-1})		
Moč	Mnichov, Německo	Pt 6.5-20	-	[87]
	Německo		ICP-MS DPV	[35]
	Obyvatelé města	Pt 3.43		
	Obyvatelé žijící v blízkosti frekv. silnic	Pt 3.27		
	Obyvatelé venkova	Pt 2.06		
Krev	Chorvatsko Česká republika Polsko Slovensko Slovinsko Švédsko	(ng.l^{-1}) Pt 0.6-5.2 Pd 5-9,.3 Rh 0.4-3.6	ICP-MS	[95]

[*] Citace a práce pod vedením autorky

4.2 PŘÍNOS – APLIKACE A VYUŽITÍ NOVÝCH SORPČNÍCH TECHNIK PŘI STUDIU KONTAMINACE ŽIVOTNÍHO PROSTŘEDÍ

Z **Tabulky 2**, která přehledně shrnuje práce zabývající se stanovením platinových kovů v environmentálních a biologických vzorcích, je patrné, že vyvinuté a inovované sorpční postupy pro prekoncentraci platinových kovů byly aplikovány pro stanovení jejich koncentrací v různých matricích. Analyzována byla znečištěná atmosféra, polétavý prach, spady v tunelech a v okolí vozovek, v půdách i na vegetaci v okolí frekventovaných dopravních komunikacích, rostlinné vzorky a říční sedimenty [80], (**Příloha 10**).

Pro potvrzení úniku PTK z automobilových katalyzátorů byl analyzován nový automobilový katalyzátor a použitý katalyzátor po ujetí 80 000 km (katalyzátory dieselových motorů). V tomto případě byly analýzy prováděny přímo (ICP-OES), bez nutnosti prekoncentračního kroku. Nový katalyzátor obsahoval v průměru 3 mg Pt na 1 gram katalyzátoru, v použitém katalyzátoru byl průměrný obsah Pr 1,7 mg.g^{-1} katalyzátoru. Za předpokladu, že celý katalyzátor váží kolem 500 g lze předpokládat, že během prvních 80 000 km provozu automobilu došlo k úniku cca 0,70 g Pt z jednoho automobilu [45]. Úniky PTK z katalyzátorů jsou největší právě během několika prvních desítek tisíc najetých kilometrů, pro Pt to je asi do 120 000 km, pro Pd do 70 000 km a pro Rh do 35 000 km [96]. Avšak ani po ujetí těchto km neztrácí katalytická vrstva svoji účinnost, emise PTK na ujetý kilometr však klesají. Přítomnost PTK byla potvrzena i přímo ve výfukových sazích, kde se pohybovaly hodnoty pro Pt v rozmezí 98-120 ng.g^{-1} a Pd 118-155 ng.g^{-1} výfukových sazí [86]. Metoda byla validována za použití standardního referenčního materiálu výfukových sazí NIES No. 8, se známým obsahem Pt, Pd, Rh, Ru a Ir [97].

Primární složkou, do které vstupují automobilové emise s platinovými kovy, je atmosféra. Při analýze ovzduší je zapotřebí mít k dispozici vzorkovače pro odběr prachových částic, kdy dochází k záchytu těchto částic na filtru ze skleněných mikrovláken, který je pak dále analyzován. Pro zachycení dostatečného množství částic je v případě platinových kovů, nasáván vzduch minimálně 24 hod. Po vyloužení v *aqua regia* jsou platinové kovy stanovovány buď přímo, metodou ICP-MS, nebo po separaci a prekoncentraci PTK metodou ICP-OES nebo ET-AAS.

Prvními vzorky, analyzovanými v r. 1999 [50], (**Příloha 3**), byly filtry z 5 meteorologických stanic ČHMÚ (Kočkov, Všechlapy, Souš, Sokolov, Měděnec), kde byly zjištěny obsahy PTK v rozmezí pro Pt 9-62 pg.m^{-3} (ICP-OES) a 13-42 pg.m^{-3} (ICP-MS) a pro Pd <LOD-280 pg.m^{-3} (ICP-OES) a <LOD-283 pg.m^{-3} (ICP-MS). Dalšími analyzovanými vzorky byly filtry umístěné ve vzorkovači v Brně (křižovatka ulic Kounicova, Kotlářská). Tam byly po analýze metodou ICP-MS nalezeny obsahy Pt v rozmezí 12-35 pg a Pd 37-61 pg v 1m^{3} prosátého vzduchu [86].

V období od 1. 11. 2012 do 31. 10. 2013 probíhal na území města Brna roční monitoring obsahu platiny v polétavém prachu [23], (**Příloha 5**). Při odběru 24 hodinových vzorků byly ve spolupráci s ČHMÚ poskytnuty filtry, získané z vysokoobjemového vzorkovače DHA-80, který byl umístěn na křižovatce ulic Údolní, Úvoz. Provoz v tomto místě je zhruba 40 000 aut za 24 hodin. Obsah Pt v polétavém prachu byl v rozmezí 61,9-2997,7 ng.g^{-1}. Tyto hodnoty byly vztaženy také na objem prosátého vzduchu a koncentrace Pt ve vzduchu v okolí této frekventované křižovatky se pohybovala v intervalu 2,3-51,5 pg.m^{-3}. Ze získaných výsledků je zřejmé, že množství zachycené platiny v polétavém prachu závisí na ročním období. Nejvyšší koncentrace ve vzduchu byly naměřeny v měsících květen, červen a červenec, kdy hodnoty koncentrace Pt byly kolem 50 pg.m^{-3}, to odpovídá téměř 3000 ng Pt v 1 g polétavého prachu. Zajímavostí ovšem je, že zrovna v tomto období byly naměřeny nejnižší hmotnosti polétavého prachu. Nejvyšší hodnoty polétavého prachu byly v lednu 2013, kdy byla na území města Brna vyhlášena smogová situace. Vysvětlením je, že k emisím PTK dochází při stejném provozu v místě odběru pořád stejnou měrou, avšak prašnost se mění dle meteorologických a rozptylových podmínek, a tím pak i výsledná hodnota koncentrace PTK v 1 g polétavého prachu.

Další, velmi zajímavou matricí pro zjištění lokální kontaminace PTK, je silniční prach. Hodnoty koncentrací platinových kovů jsou zde oproti ostatním matricím mnohonásobně vyšší, v případě vzorků odebraných z míst chráněných před meteorologickými vlivy (podjezdy, tunely) pak i řádově vyšší. Právě v tunelovém prachu byly PTK poprvé nalezeny již v 90. letech 20. století a již tehdy byly považovány za potenciální environmentální riziko. Vlivem dešťů nebo při čištění tunelů se pak dostávají do splachů ze silnic a stávají se tak součástí městských odpadních vod.

V začátcích výzkumu obsahu PTK v silničním prachu byly zjištěny hodnoty koncentrace na území města Brna pro Pt v rozmezí 2,8-503 ng.g^{-1} prachu a pro Pd v intervalu 11-40 ng.g^{-1} prachu [86]. Z výsledků je patrné, že emise PTK jsou v částicové podobě (nanočástice nebo mikročástice, povrchově oxidované částice nebo částice vázány na pevné částice výfukových emisí) a jejich výskyt v silničním prachu je nehomogenní.

Důležitým materiálem v oblasti environmentální analýzy jsou vzorky půd ze znečištěných oblastí. V období 9/2014-1/2015 probíhalo na území města Brna monitorování obsahu Pt v půdních vzorcích z okolí frekventovaných dopravních komunikací. Byly nalezeny obsahy Pt v rozmezí 10,23-100,8 ng.g^{-1} půdy [93]. Tento výzkum pokračoval dále (9/2016-11/2016) i s ohledem na odběr vzorků půd z různých vzdáleností od dopravní komunikace. Do 1 m od silnice byly nalezeny obsahy Pt v intervalu 37,10-186,1 ng.g^{-1} půdy a Pd 20,51-85,50 ng.g^{-1} půdy. Ve vzdálenosti 5 m od komunikace byly nalezeny již nižší obsahy, pro Pt 5,213-10,17 ng.g^{-1} půdy a Pd 10,81-11,34 ng.g^{-1} půdy. Ve vzdálenostech delších než 5 metrů byly obsahy Pt a Pd již pod limitem detekce použité metody stanovení [71].

V letech 2015-2016 proběhl na území města Brna výzkum distribuce platiny v environmentálních vzorcích [25], (**Příloha 6**). Analyzovány byly vzorky tunelového a silničního prachu, půda a vegetace v okolí frekventovaných komunikací. Množství Pt v tunelovém prachu dvou tubusů Pisáreckého tunelu (510 m), Husovického tunelu (580 m) a Královopolského tunelu (1250 m), s hustotou automobilové dopravy cca 40 000 aut za 24 hodin, se pohybovalo v době před čištěním tunelů v rozmezí 66,3-192 ng.g^{-1} prachu a měsíc po čištění tunelů v intervalu 29,2-38,2 ng.g^{-1} prachu. Nejvyšší hodnoty pak byly nalezeny v nejdelším, Královopolském tunelu. Tunelový prach byl odebírán přímo na komunikaci i ze stěn tunelu. Zajímavostí také je, že byly analyzovány oplachové vody, získané po čištění tunelů. V těchto vodách bylo nalezeno detekovatelné množství rozpuštěné platiny, v koncentracích v rozsahu jednotek ng.l^{-1}.

Množství Pt nalezené v půdách v těsné blízkosti silnic bylo v rozmezí 10,5-15,7 ng.g^{-1} půdy a v travní vegetaci odebrané na stejném místě se koncentrace platiny pohybovala v rozmezí 10,0-11,6 ng.g^{-1}. Z výsledků je patrné, že v tunelech dochází k postupnému zvyšování koncentrace platiny, množství Pt v půdách a okolní vegetaci pak koreluje s hustotou automobilové dopravy v daném místě. Odebrané vzorky půd a trávy byly rozděleny do tří kategorií: 1. komunikace s vysokou hustotou automobilové dopravy (40 000 aut/24 hod), 2. silnice se střední zátěží (20 000/24 hod) a 3. místní komunikace s nízkou dopravní hustotou (1 000 aut/24 hod). Výběr vzorkovacích míst byl prováděn jednak s ohledem na hustotu automobilové dopravy a také s ohledem na přítomnost pásu travní vegetace, nacházející se v těsné blízkosti silnice. Průměrné hodnoty obsahu Pt byly u 1. kategorie vzorků 12,8 ng.g^{-1} půdy a 10,6 ng.g^{-1} travní vegetace, u 2. kategorie 7,3 ng.g^{-1} půdy a 6,5 ng.g^{-1} travní vegetace a pro 3. kategorii 5,5 ng.g^{-1} půdy a 4,3 ng.g^{-1} trávy. Zároveň byly analyzovány vzorky půd a trávy v oblastech bez automobilové dopravy (Lužánecký park, Mariánské údolí, Lom Líšeň), nalezené obsahy Pt zde byly pod mezí detekce, přesto, že byla použita prekoncentrační technika (stejně jako o všech ostatních analýz v této práci).

Zajímavým analytem jsou také říční sedimenty. V roce 2018 proběhl na řece Svratce monitoring obsahu Pt a Pd v říčním sedimentu [31]. Vzorkovací místa se nacházela vždy u mostů s dopravní komunikací, vedoucích přes řeku Svratku. Bylo vytipováno 8 odběrových míst a odběry vzorků probíhaly vždy na levé a pravé straně koryta řeky (bráno ve směru toku řeky) vždy přímo pod mostem a pak ve vzdálenostech 50 m a 100 m. Na jednom odběrovém místě tak bylo odebráno vždy 6 vzorků sedimentů. Koncentrace Pt se v říčním sedimentu pohybovala mezi 8,839-48,82 ng.g^{-1} sedimentu a pro Pd v intervalu mezi 1,800-7,674 ng.g^{-1} sedimentu. Při odběrech sedimentů se v jednom odběrovém místě podařilo odebrat i schránky již odumřelých měkkýšů škeble říční (*Anodonta anatina*). Nalezené obsahy Pt ve schránce měkkýše byly 11,72-21,68 ng.g^{-1} a v okolním sedimentu 24,60-27,65 ng.g^{-1}. Koncentrace Pd stanovená ve schránce měkkýše byla 2,986-5,395 ng.g^{-1} a v okolním sedimentu 0,99-2,90 ng.g^{-1}. Ze získaných výsledků je patrné, že palladium, se svojí schopností bioakumulace, bylo ve schránkách měkkýše nalezeno ve vyšší koncentraci než v okolním sedimentu, na rozdíl od platiny, která ve schránkách byla nalezena také, ale spíše v koncentracích nižších, než její hodnota v okolním sedimentu. Byl tedy prokázán vstup PTK do vodních živočichů a v případě Pd tak i jeho bioakumulace.

Další výzkum v oblasti analýzy environmentálních vzorků byl zaměřen na studium a výběr vhodných bioindikátorů pro hodnocení úrovně kontaminace životního prostředí platinovými kovy [28], **Příloha 7**. Jako bioindikátory byly testovány lišejník terčovka zední (*Xanthoria parietina*), mech travník Scherberův (*Pleurozium schreberi*) a jehličí borovice černé (*Pinus nigra*). V prvotních experimentech byla zjišťována na neznečištěných vzorcích bioindikátorů (odběr v NP Šumava, obsah Pt a Pd <LOD) jejich sorpční kapacita pro Pt a Pd za laboratorních podmínek. Lišejníky byly vyhodnoceny jako nejlepší bioindikátor s největší sorpční kapacitou pro Pd i Pt. Následovaly mechy a nejmenší sorpční kapacitu pro Pt a Pd vykazovalo jehličí. Pokusy

byly prováděny v nepřítomnosti a přítomnosti 0,1 mol.dm^{-3} HCl. Sorpce v kyselém médiu byla zvolena z důvodu potlačení ztrát PTK v sorbovaných roztocích, které se ve velmi nízkých koncentracích snadno sorbují na stěny použitého laboratorního nádobí. Aby se zabránilo této sorpci, je třeba roztoky okyselit taky, aby se PTK převedly na rozpustné chlorokomplexy. V tomto případě dochází k účinnější sorpci ve všech případech v kyselém prostředí. To samozřejmě souvisí také s pohyblivostí a biologickou dostupností platinových kovů při nižších hodnotách pH. Při environmentálních hladinách koncentrací PTK však kapacitně postačují všechny tři druhy bioindikátorů, tedy i nižší sorpční kapacity mechu a jehličí.

Původní předpoklad, že lišejníky budou vykazovat nejlepší sorpční kapacitu z vybraných bioindikátorů, se potvrdil. Jejich vysoká sorpční schopnost je způsobena tím, že povrch jejich těla není pokryt kutikulou nebo jiným ochranným prvkem (vrstva tuků a vosků) a jsou tak schopny sorbovat kontaminanty z atmosféry celou plochou svého těla. Výhodou je i jejich dlouhověkost, nenáročnost a přizpůsobivost okolním podmínkám. Relativně menší sorpční schopnost než lišejníky vykazovaly mechy. Mechy jsou velmi rozšířené, což z nich činí velmi populární bioindikátory. Ačkoli jejich nadzemní orgány nejsou pokryty ochrannou vrstvou a sloučeniny kovů tak mohou proniknout přímo do buněčné stěny, nemohou překročit svou sorpční kapacitu. Jsou ovšem náchylné na nedostatek vzdušné vlhkosti. Nejméně vhodné je pro bioindikaci platinových kovů jehličí, protože jeho povrch je pokryt silnou kutikulou s kutikulárním voskem, takže sorpce anorganických kontaminantů je touto bariérou významně omezena a jejich použití je vhodnější spíše pro stanovení organických kontaminantů.

Po otestování sorpčních kapacit byly analyzovány vzorky lišejníků, mechů a jehličí na vybraných 5 lokalitách na území města Brna pro zjištění úrovně kontaminace a 1 vzorek srovnávací, z místa bez automobilové dopravy (Horní Lažany, Vysočina). Vzorky byly odebírány v těsné blízkosti komunikace 1. třídy s frekvencí automobilové dopravy několika 10 000 aut/24 hodin. Lokalizace těchto odběrových míst byla poměrně náročná, protože základním požadavkem bylo, aby se v tom stejném místě vyskytovaly jak lišejníky, tak mechy a jehličí. Obsahy Pt se pohybovaly v rozmezí <LOD-23,18 ng.g^{-1} lišejníku, <LOD-59,40 ng.g^{-1} mechu a <LOD-7,278 ng.g^{-1} jehličí. Obsahy Pd byly nalezeny v intervalu 5,140-47,08 ng.g^{-1} lišejníku, 2,979-8,449 ng.g^{-1} mechu a 3,017-12,09 ng.g^{-1} jehličí. Vyšší naměřené koncentrace palladia v lišejnících jsou způsobeny jeho biologickou dostupností, která se zvyšuje v pořadí Pd> Pt $\geq$ Rh a odpovídá i jiným studiím [98]. Biologická dostupnost úzce souvisí s rozpustností a pohyblivostí prvku. Palladium má nejlepší potenciál pro transformaci na rozpustnější biologicky dostupné sloučeniny po vstupu do životního prostředí. Na druhé straně platina, která je méně biologicky dostupná, se ukládá spíše na povrchu bioindikátoru. Množství zachycené platiny je proto silně ovlivněno povětrnostními podmínkami a atmosférickými srážkami. Bylo potvrzeno, že nejrozpustnější a nejmobilnější v životním prostředí a s největším potenciálem absorbovat se do organismu je palladium.

Proto i nejnovější práce se zaměřila právě na palladium a jeho stanovení ve zvoleném bioindikátoru, lišejníku terčovka bublinatá (*Hypogymnia physodes*) [60], **Příloha 9**. V této práci byla použita metoda aktivního „bag“ biomonitoringu. Nekontaminovaný bioindikátor, odebraný z prostředí mimo automobilovou dopravu (CHKO Beskydy), byl umístěn do „tašky“ z prodyšné síťky a úmyslně vystaven automobilovým imisím. Jednalo se tedy o aktivní expoziční akumulační bioindikaci. Metoda je použitelná i pro mechy, ty jsou ale náchylnější na vysychání a musí se vytvořit podmínky s uměle vlhčeným substrátem. Takto připravené vzorkovače byly umístěny na svodidla v bezprostřední blízkosti komunikací. Bylo vybráno 9 míst na území města Brna s vysokou zátěží automobilové dopravy a 1 srovnávací místo mimo dopravní komunikaci. Na jedno místo byly přichyceny vždy 3 „tašky“ s lišejníky proto, aby se mohla sledovat doba expozice. První vzorkovače byly odebrány po 90 dnech, druhé vzorkovače po 120 dnech a třetí po 150 dnech expozice v jednom stejném místě. Byla zvolena také místa s různou hustotou dopravy tak, aby se mohl posoudit vliv hustoty automobilové dopravy na množství Pd zachyceného v bioindikátoru. Jednalo se o tato místa: dálnice D2 (50 000 aut/24 hod), ulice Sportovní (45 000 aut/24 hod), Tomkovo náměstí (40 000 aut/24 hod), ulice Hradecká (směrem do centra) a ulice Otakara Ševčíka (35 000 aut/24 hod), ulice Hradecká směrem z města (25 000 aut/24 hod), ulice Koliště a Poříčí (20 000 aut/24 hod) a ulice Kotlářská (15 000 aut/24 hod). Po 90 dnech bylo ve vzorcích lišejníků stanoveno množství Pd v rozsahu 5,775-8,456 ng.g^{-1}, po 120 dnech 9,160-14,57 ng.g^{-1} a po 150 dnech 12,34-23,58 ng.g^{-1}. Byl tedy jednoznačně potvrzen nárůst zachyceného palladia v závislosti na době expozice. Ze získaných výsledků je dále patrné, že množství zachyceného Pd přímo souvisí s hustotou automobilové dopravy. Z těchto dat byla sestavena závislost nárůstu obsahu Pd v bioindikátorech s ohledem na hustotu dopravy, pro možnou predikci znečištění. Se znalostí počtu projetých aut za den lze podle této závislosti spočítat přibližné zatížení biologických vzorků v těsné blízkosti dopravní komunikace.

5 NANOČÁSTICE PLATINY

5.1 SOUČASNÝ STAV PROBLEMATIKY NANOČÁSTIC PLATINOVÝCH KOVŮ V ŽIVOTNÍM PROSTŘEDÍ

Nanomateriál je definován jako částice přírodního (natural nanoparticles, NNPs), antropogenního nebo cíleně vyráběného průmyslového původu (engineered nanoparticles, ENPs), které mají v libovolném směru rozměr v řádu nanometrů (1-100 nm). Nanočástice a nanomateriály jsou přirozenou součástí životního prostředí. V půdách se jedná především o jílové minerály, oxidy a hydroxidy kovů a huminové látky, vyskytující se však často ve shlucích. Podle práce [99] je půda velmi složitým systémem směsi různých typů nanočástic, ve kterém se všechny transportní procesy odehrávají v nano měřítku.

V současnosti vzrůstá produkce a využití průmyslově vyráběných nanočástic ve všech oborech lidské činnosti a kontaminace životního prostředí je tak téměř nevyhnutelná. Nanočástice nevznikají pouze jako cílený produkt, ale také jako nežádoucí produkt jiného procesu. Tyto antropogenní nanočástice se stávají např. součástí emisí ze spalovacích procesů (spalování biomasy, fosilních paliv, odpadů). Dalšími zdroji nanočástic v životním prostředí jsou kromě automobilové dopravy také lékařství, těžařský průmysl a chemický průmysl.

Významnou skutečností jsou odlišné vlastnosti nanočástic a částic téhož materiálu v makroskopické formě. Jedná se zejména o toxikologické a fyzikálně-chemické vlastnosti. Jako příklad lze uvést právě platinu, která je ve své makropodobě považována za biokompatibilní (výroba endoprotéz, kardiostimulátorů). Nanočástice platiny jsou naopak velmi nebezpečné, zejména díky svým katalytickým vlastnostem, snadno přechází přes buněčnou membránu a při vdechnutí působí v plicích toxicky [100].

Jak již bylo popsáno výše, celosvětová produkce prvků skupiny platinových kovů neustále roste. Masové využití platiny v autokatalyzátorech představuje více jak 50 % roční poptávky po platině. Povinná instalace katalyzátorů v motorových vozidlech výrazně snížila emise škodlivých výfukových plynů tak, aby mohly být splněny požadované emisní limity, ale vedla k zvýšenému uvolnění platinových kovů do životního prostředí a některé studie přímo prokázaly uvolňování Pt ve formě nanočástic (NPs) [101-103].

Koncentrace Pt ve vzorcích životního prostředí jako je silniční prach, půda, povrchová voda, sedimenty a rostliny se v posledních desetiletích významně zvýšila (viz kapitola **Platinové kovy v životním prostředí**). Ještě vyšší koncentrace Pt pak byly nalezeny v tunelovém prachu. Koncentrace nanočástic Pt ve vodních ekosystémech je však dosud relativně nízká ve srovnání s jejich koncentrací v bezprostřední blízkosti silnic. Několik studií již ale uvádí toxicitu platinových nanočástic pro vodní organismy [104-105].

Komplexy platiny (např. Cisplatina, Carboplatina) se používají již řadu desítek let pro účinnou léčbu rakoviny, jejich nevýhodou však je jejich vysoká toxicita. Proto byly studovány a nalezeny některé další sloučeniny platiny na bázi nanočástic, které jsou cytostaticky velmi účinné [106] a jejich cytotoxicita je nižší [107]. Většina těchto léčiv obsahujících Pt komplexy se vylučuje močí pacientů (asi 70 %) a vstupuje do systémů odpadních vod [12]. Metody odstraňování těchto látek nejsou k dispozici, což přispívá k další environmentální kontaminaci.

V současné době nejsou známy téměř žádné informace o environmentálním chování nanočástic platiny, jako je např. jejich agregace, rozpouštění, reakce se sloučeninami obsahujícími síru, reakce s přírodní organickou hmotou, možná adsorpce na biologickém povrchu, sedimentace, depozice a persistence v přírodních podmínkách. Právě tyto fyzikálně-chemické procesy mohou významně měnit a ovlivnit environmentální chování nanočástic, jejich vstup do jednotlivých složek životního prostředí, biodostupnost a toxicitu a určit jejich další osud v životním prostředí [108]. Jejich chování v životním prostředí se zatím pouze předpokládá, a to na základě studia chování některých běžnějších a vědecky probádanějších nanočástic těžkých kovů jako je například zlato [109] nebo stříbro [110]. Teprve některé současné studie se snaží o zlepšení pochopení environmentálního chování platinových nanočástic [111]. Většina současného výzkumu nanočástic platinových kovů je však spíše směřována do oblasti medicíny, biomedicíny a také do oblasti „zelené syntézy“ nanočástic platiny, s využitím bakterií, hub, řas nebo rostlin pro biogenní syntézu nanočástic Pt [112-113].

V **Tabulce 3** je uveden přehled několika málo prací, které se problematikou nanočástic Pt zabývají, s uvedením oblasti, ve které probíhá výzkum. Těchto prací není doposud příliš mnoho a jsou spíše věnovány zdrojům NPs, jejich přípravě a výrobě a použití. Méně prací se pak věnuje výzkumu v oblasti chování nanočástic Pt za environmentálních podmínek a neexistují žádné práce, které by zkoumaly vliv NPs Pt na fyzikálně-chemické vlastnosti složek životního prostředí, např. půd.

Tabulka 3 Přehled prací zabývajících se problematikou nanočástic v životním prostředí

Druh NPs	Výskyt	Studovaná problematika	Literatura
Antropogenní	Atmosféra Hydrosféra	Automobilové emise	[103]
Antropogenní Průmyslové	Antroposféra Biosféra	Cesty vstupu do ekosystémů Predikce a měření v přírodních ekosystémech Osud v životním prostředí Toxicita	[108]
Průmyslové Antropogenní	Biosféra	Příprava a charakterizace Pt NPs Koloidní stabilita Ekotoxikolgie	[111]
Antropogenní Průmyslové	Atmosféra Biosféra	Zdroje NPs Environmentální nanotechnologie Nanočástice v energetice Environmentální vlivy a toxicita	[114]

Přírodní Antropogenní Průmyslové	Atmosféra	Vlastnosti Stanovení a charakteristika Význam v atmosféře	[115]
Přírodní Antropogenní Průmyslové	Antroposféra	Klasifikace Zdroje NPs a vliv na zdraví Toxikologie Aplikace	[116]
Přírodní	Pedosféra	NPs v půdách Charakterizace a frakcionace	[117]
Přírodní	Atmosféra Hydrosféra Pedosféra Biosféra	Vlastnosti Identifikace v půdách a vodě Vliv na kvalitu půdy Pozitivní role NPs Environmentální rizika NPs	[118]
Průmyslové	Pedosféra Biosféra	Charakterizace, stanovení a monitoring NPs Příprava vzorků pro stanovení NPs	[119]
Průmyslové Antropogenní	Pedosféra	Vliv Pt NPs na půdní organickou hmotu	[120]*

*Citace a práce pod vedením autorky

5.2 PŘÍNOS - OBJASNĚNÍ CHOVÁNÍ NANOČÁSTIC PLATINY V PŮDNÍM PROSTŘEDÍ

Jak již bylo řečeno v předcházející kapitole, shrnující současný stav problematiky nanočástic platiny v životním prostředí, doposud byl přehlížen možný vliv těchto nanočástic na fyzikálně-chemické procesy v jednotlivých složkách životního prostředí. Platina a vliv jejich sloučenin na složky životního prostředí se studuje již delší dobu, ale nanočásticím platiny doposud nebyla věnována dostatečná pozornost. Podle celé řady studií jsou ale vlastnosti materiálů v nano oblasti zcela odlišné od jejich vlastností v mikro a makro podobě, nejinak je tomu i u nanočástic Pt.

Pro pochopení chování nanočástic Pt v půdách byl, jako první svého druhu, v práci [120] (**Příloha 11**), pilotně studován vliv nanočástic platiny na fyzikálně-chemické vlastnosti modelové půdní organické hmoty a půdní vody. V této práci se vycházelo z předpokladu, že Pt vstupuje do životního prostředí jednak přímo ve formě nanočástic (primární), ale také jako mikročástice. Za environmentálních podmínek dochází k jejich rozpadu, tj. „erozi“, vznikají sekundární nanočástice. Reaktivita primárních i sekundárních nanočástic, především s velikostí pod 10 nm [121], se projevuje velmi silnou hydratací. Vzhledem k tomu, že celá řada půdních procesů probíhá v nano rozměrech a nano-kavitách, přítomnost větších koncentrací nanočástic může zásadně ovlivnit i makroskopické jevy.

Tato problematika však není, s ohledem na životní prostředí, doposud prozkoumána. Během zpracování naší publikace byly nalezeny další odborné práce, které poukazovaly na to, že některé nanočástice silně ovlivňují makroskopické fyzikálně-chemické vlastnosti vody. Tohoto efektu se využívá např. v hasebních prostředcích [122], kde podporují rychlejší odpařování vody z rozprašovaných mikrokapiček. Pro pochopení vlivu Pt NPs na půdní organickou hmotu byly v naší práci podrobně studovány vlivy širokého rozmezí hodnot koncentrací NPs na modelovou půdní organickou hmotu. Jedním z cílů bylo nalezení hraniční koncentrace Pt způsobující negativní vlivy v půdě a jejich porovnání s reálnými koncentracemi antropogenně vstupujících nanočástic platiny. Pro studium byly zvoleny komerčně dodávané nanočástice platiny ve vodě o velikosti 3 nm. Tento rozměr byl zvolen s ohledem na fakt, že NPs emitované z autokatalyzátorů mají průměrný rozměr v rozsahu 0,3 μm – 25 nm [102] a ty se dále rozpadají na menší částice, jež mohou být snadněji rozpustné v organických kyselinách [123] a stát se tak biodostupnějšími pro živé organismy. Porovnáním koncentrací Pt NPs použitých v této modelové studii s koncentracemi Pt nacházejícími se v životním prostředí byl zjištěn koncentrační překryv, který umožnil posoudit možný reálný vliv nanočástic platiny na problematiku vody za environmentálních podmínek.

V práci byl studován především vliv těchto NPs na schopnost půdy zadržovat vodu, pevnost vazby mezi vodou a půdou, stabilitu vodních molekulárních můstků a interakce s alifatickými krystality. Bylo zjištěno, že silná hydratace nanočástic způsobuje stabilizaci struktur vodních můstků, která má za následek zvýšení rigidity fyzikální struktury půdní organické hmoty. Dále pak bylo zjištěno, že u větších objemů (například v pórech) snižují Pt nanočástice výparnou entalpii vody tím, že porušují strukturu vody. Výsledkem je, že platinové nanočástice podporují zrychlené vysychání půdy. Navíc při vysoké koncentraci indukují krystalizaci alifatických krystalitů. Bylo tedy zjištěno, že nanočástice Pt ovlivňují lokální fyzikálně-chemické procesy v půdách a mohou následně přispět ke zvýšení evapotranspirace a zhoršení funkcí půdy.

V současné době pokračuje další výzkum v této oblasti, a to především studiem vlivu velikosti nanočástic na uvedené parametry. Dále je pak plánováno i studium osudu Pt nanočástic v půdách, jejich vliv na půdní mikrobiologické procesy, sorpční schopnosti a obecné půdotvorné procesy (agregace, stabilizace organického uhlíku).

Dá se říci, že touto publikací tak byla otevřena zcela nová kapitola zaměřená na problematiku vlivu nanočástic na fyzikálně-chemické procesy ve složkách životního prostředí. Jak naznačují materiálově orientované studie [122], pro výše popsaný vliv nanočástic Pt na vodu se může jednat o obecný jev všech druhů nanočástic, a to včetně uhlíkatých materiálů. Takto zaměřený výzkum tak doplní informace o vlivu nanočástic na živé systémy [124]. Výsledkem plánovaného výzkumu by měl být jak komplexní environmentální pohled na rizika spojená s nechtěnými emisemi nanočástic, tak na rizika spojená s jejich záměrným používáním při ochraně životního prostředí a v zemědělství.

6 ZÁVĚRY A VIZE DO BUDOUCNA

Z výše uvedených faktů a výsledků výzkumu v oblasti kontaminace životního prostředí platinovými kovy je zřejmé, že se jedná o celosvětový problém. Důsledky vyplývající z používání platinových kovů jsou nejen lokální, ale i globální, ať už jde o jejich přírodní zdroje, použití v průmyslových aplikacích, v automobilovém průmyslu, využití v lékařství a nakládání s odpady a s odpadními vodami. Emisní limity exhalací z automobilových zdrojů se na celém světě neustále zpřísňují a nezbytné používání platinových kovů pro snižování automobilových emisí přispívá k vzestupnému trendu jejich spotřeby a antropogennímu vstupu do životního prostředí na celosvětové úrovni.

Nejvhodnější metodou pro přímé stanovení platinových kovů v environmentálních vzorcích je technika ICP-MS, která je vysoce citlivá s možností simultánní víceprvkové analýzy. Ultrastopové hodnoty platinových kovů lze však také stanovit atomovou absorpcí (ET-AAS), atomovou emisí (ICP-OES) nebo elektrochemickými metodami (voltametrické techniky). Stopové koncentrace platinových kovů v environmentálních a biologických vzorcích často vyžadují vhodné metody a postupy pro jejich separaci a prekoncentraci před vlastním analytickým stanovením. Nejčastěji se využívá technika extrakce do tuhé fáze (SPE) a jako sorbenty se používají modifikované hydrofobní sorbenty nebo aniontoměniče. Nově se také používají sorbenty typu nanotrubiček a nanovláken, často upravené modifikací pro zvýšení sorpční selektivity platinových kovů. Při použití prekoncentrační techniky je vždy nutné vzít v úvahu všechny relevantní faktory, jako je typ vzorku, metoda rozkladu vzorku, možný matricový efekt a interference, typ a druh eluentu, sorpční kapacita, prekoncentrační faktor a instrumentální analytická technika konečné detekce s požadovaným detekčním limitem.

Při stanovování ultrastopových koncentrací platinových kovů existuje mnoho dalších výzev a neprobádaných oblastí, zejména s ohledem na jejich vstup do životního prostředí ve formě reaktivních nanočástic, jejichž problematika je v současné době ve fázi výzkumu, a skutečnosti, že oxidační stav, speciace a forma výskytu významně ovlivňují jejich reaktivitu, biologickou dostupnost a toxické vlastnosti, jež však nejsou dosud zcela prostudovány. Do těchto oblastí směřuje současný výzkum.

Je třeba zmínit i další důležitou a zároveň i překvapující skutečnost. Při oponentním řízení článku (Příloha 10) měli oba oponenti námitku, že v článku chybí krátký literární výzkum a prognóza o nových dopravních koncepcích a nových automobilových motorizacích, hybridních (HEV), hybridních plug-in (PHEV) a plně elektrických automobilech (BEV). Žádný z těchto konceptů však nezaručuje tak vysokou účinnost a bezpečnost celého procesu jako spalovací motor. Spalovací motory tak dosud mají mnoho nesporných výhod a nejen z těchto důvodů nebude pravděpodobně jejich výroba v brzké době významně omezena, a to i přes úpornou snahu o jejich diskvalifikaci legislativními zásahy. Jejich kvalita, výkonnost, bezpečnost provozu, cenová dostupnost a časová udržitelnost a zejména takřka neomezená mobilita hovoří stále v jejich prospěch.

Používání platinových kovů v následujících letech v nově vyrobených automobilech a i v těch stávajících tak zcela jistě nebude klesat a jejich emise do životního prostředí z těchto mobilních zdrojů budou pokračovat. V současné době je celosvětově v provozu 1,3 miliardy osobních automobilů s průměrným meziročním nárůstem prodeje 4 %. V roce 2017 byla překonána hranice prodeje 90 milionů automobilů za rok. V ČR bylo v roce 2018 v provozu 5,59 milionů osobních automobilů a prodeje neustále narůstají v souladu s celosvětovým vývojem.

Stejně tak v oblasti medicíny pokračuje neustále nový výzkum ve využívání nanočástic platiny, zejména pro jejich antibakteriální, antioxidační, antifungální, cytostatické a cytotoxické účinky. Jsou studovány nové biogenní postupy přípravy nanočástic jako alternativní, ekonomický a ekologický přístup ve srovnání s konvenčními fyzikálně-chemickými metodami přípravy NPs.

Platinové kovy nás tak pro jejich excelentní vlastnosti, jaké nemají u ostatních prvků a jejich sloučenin obdoby, budou provázet neustále ve všech možných oborech lidské činnosti. Jejich problematika tak z hlediska negativního vlivu na všechny složky životního prostředí zůstává neustále otevřená…

7 SEZNAM POUŽITÝCH ZKRATEK

8HQS	8-hydroxychinolin-5-sulfonová kyselina
AdSV	adsorpční katodická stripovací voltametrie
Ajatin®	benzyldimethyl(dodecyl)ammonium bromid
APDC	ammoniumpyrolidindithiokarbamát
AR	*aqua regia* ($HCl:HNO_3$ 3:1)
BCR®	certifikovaný referenční materiál
BEV	Battery Electric Vehicle, elektrická vozidla jen s baterií jako zdrojem energie
Bond-Elut C18®	octadecyl modifikovaný silikagel
CAdCSV	katalytická adsorpční katodická stripovací voltametrie
CMDCT	bis(carboxylmethyl)dithiokarbamát
CNF/PEI	celulózová nanovlákna modifikovaná polyethyleniminem
CPC	1-hexadecylpyridinium chlorid
CRM	certifikovaný referenční materiál
CTAC	hexadecyl(trimethyl)ammonium chlorid
CZE	kapilární zónová elektroforéza
ČHMÚ	Český hydrometeorologický ústav
DKTS APSG	silikagel modifikovaný difenylketonmonothiosemikarbazonem
DMG	dimethylglyoxim
DMG SG	silikagel modifikovaný dimethylglyoximem
DPTH-gel	1,5-bis(di-2-pyridyl)methylen thiokarbohydrazid
DPV	diferenční pulsní voltametrie
ENPs	průmyslově vyráběné nanočástice (engineered nanoparticles)
ET-AAS	atomová absorpční spektrometrie s elektrotermickou atomizací
EURO	emisní norma
FAAS	plamenová atomová absorpční spektrometrie
FTIR	infračervená spektrometrie s Fourierovou transformací
HEV	Hybrid Electric Vehicle, automobily s hybridním pohonem, tvoří je elektromotor a benzinový nebo dieselový motor, baterie se nabíjí během jízdy pomocí generátoru, a to buď přes motor, nebo rekuperací z brzdění
HMImT	1-hexyl-3-methylimidazol-2-thion
HPLC	vysokoúčinná kapalinová chromatografie
HR-CS-GF-AAS	atomová absorpční spektrometrie s elektrotermickou atomizací a kontinuálním zdrojem záření
ICP-AES	atomová emisní spektrometrie s indukčně vázaným plazmatem
ICP-MS	hmotnostní spektrometrie s indukčně vázaným plazmatem
ICP-OES	optická emisní spektrometrie s indukčně vázaným plazmatem
ILs	iontové kapaliny (Ionic Liquids)
LOD	mez detekce (Limit Of Detection)
LOQ	mez stanovitelnosti (Limit Of Quantification)
MW	rozklad v mikrovlnné peci

MWCNTs	uhlíkové nanotrubičky
NNPs	přírodní nanočástice (natural nanoparticles)
NPs	nanočástice (nanoparticles)
PAMAM SG	polyamidoamin imobilizovaný na silikagelu
PAN-TU-GA	polyakrylonitril modifikovaný thiomočovinou a glutaraldehydem
PAR	4-(2-pyridylazo) resorcinol
PEI	polyethylenimin
PHEV	Plug-in Hybrid Electric Vehicle, hybridní plug-in automobily, mají elektrický motor napájený prostřednictvím externě nabíjené baterie ze zásuvky a spalovací motor, který se aktivuje v případě potřeby; v případě, že je aktivován spalovací motor, baterie se nabíjí rekuperací, tj. energií z brzdění
PSTH	1,5-bis(2-pyridyl)-3-sulfofenyl methylen thiokarbonohydrazid
PTK	platinové kovy
QuadraSil™ TA	silikagel modifikovaná triaminem
RF-OPT	radiofrekvenční kyslíkové plazma
RTILs	iontové kapaliny kapalné při laboratorní teplotě (Room-temperature Ionic Liquids)
SAX	silikagel modifikovaný kvartérní aminoskupinou
SBA	silikagel modifikovaný thiolovou skupinou
Septonex®	(α-carbethoxypentadecyl)trimethylammonium bromid
SDVB	styren divinylbenzen
SPE	extrawkce do tuhé fáze (Solid Phase Extraxtion)
SRM	standardní referenční materiál
Sterinol®	benzyl(dodecyl)dimethylammonium bromid
Strata C18-E®	octadecylmodifikovaný silikagel, endcapped
Strata SDB-L®	styrene divinylbenzene sorbent
TTAB	trimethyl(tetradecyl)ammonium bromid
TU	thiomočovina
XAD-4®	polystyren-divinylbenzenová pryskyřice
Zephyramin®	benzyldimethyltetradecylammonium chlorid
WHO	světová zdravotnická organizace

8 SEZNAM CITOVANÉ LITERATURY

[1] REITH, F., S.G. CAMPBELL, A.S. BALL, A. PRING a G. SOUTHAM. Platinum in Earth surface environments. Earth-Science Reviews. 2014, 131, 1-21. DOI: https://doi.org/10.1016/j.earscirev.2014.01.003. ISSN 0012-8252. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0012825214000063

[2] Johnson Matthey [online]. Hertfordshire: Johnson Matthey, 2018 [cit. 18.10.2019]. Dostupné z: http://www.platinum.matthey.com

[3] MUDD, Gavin, Simon JOWITT a Timothy WERNER. Global platinum group element resources, reserves and mining – A critical assessment. Science of The Total Environment. 2018, 622-623, 614-625. DOI: https://doi.org/10.1016/j.scitotenv.2017.11.350. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969717334083

[4] DING, Yunji, Shengen ZHANG, Bo LIU, Huandong ZHENG, Chein-chi CHANG a Christian EKBERG. Recovery of precious metals from electronic waste and spent catalysts: A review: A review. Resources, Conservation and Recycling. 2019, 141, 284-298. DOI: https://doi.org/10.1016/j.resconrec.2018.10.041. ISSN 0921-3449. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0921344918304166

[5] BENCS, L., K. RAVINDRA a R. VAN GRIEKEN. Platinum: Environmental Pollution and Health Effects: Environmental Pollution and Health Effects. Burlington: Elsevier, 2011, s. 580-595. DOI: https://doi.org/10.1016/B978-0-444-52272-6.00602-4. ISBN 978-0-444-52272-6. Dostupné také z: http://www.sciencedirect.com/science/article/pii/B9780444522726006024

[6] RAUCH, Sebastien, Harold HEMOND, Carlo BARBANTE, Masanori OWARI, Gregory MORRISON, Bernhard PEUCKER-EHRENBRINK a Urban WASS. Importance of automobile exhaust catalyst emissions for the deposition of Platinum, Palladium and Rhodium in the Northern hemisphere. Environ. Sci. Technol. 2005, 39(21), 8156-8162.

[7] KIELHORN, Janet, Christine MELBER, Detlef KELLER a Inge MANGELSDORF. Palladium – A review of exposure and effects to human health. International Journal of Hygiene and Environmental Health. 2002, 205(6), 417-432. DOI: https://doi.org/10.1078/1438-4639-00180. ISSN 1438-4639. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S1438463904701741

[8] EK, Kristine, Gregory MORRISON a Sebastien RAUCH. Environmental routes for platinum group elements to biological materials—a review. Science of The Total Environment. 2004, 334-335, 21-38. DOI: https://doi.org/10.1016/j.scitotenv.2004.04.027. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969704003511

[9] RAVINDRA, Khaiwal, László BENCS a René VAN GRIEKEN. Platinum group elements in the environment and their health risk. Science of The Total Environment. 2004, 318(1), 1-43. DOI: https://doi.org/10.1016/S0048-9697(03)00372-3. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969703003723

[10] WISEMAN, Clare a Fathi ZEREINI. Airborne particulate matter, platinum group elements and human health: A review of recent evidence: A review of recent

evidence. Science of The Total Environment. 2009, 407(8), 2493-2500. DOI: https://doi.org/10.1016/j.scitotenv.2008.12.057. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969709000138

[11] ANNESOFIE, Faurschou, Menné TORKIL, Johansen D. a Thyssen P. Metal allergen of the 21st century—a review on exposure, epidemiology and clinical manifestations of palladium allergy. Contact Dermatitis. Wiley/Blackwell (10.1111), 2011, 64(4), 185-195. DOI: 10.1111/j.1600-0536.2011.01878.x. ISSN 0105-1873. Dostupné také z: https://doi.org/10.1111/j.1600-0536.2011.01878.x

[12] PAWLAK, Justyna, Elżbieta ŁODYGA-CHRUśCIńSKA a Jakub CHRUSTOWICZ. Fate of platinum metals in the environment. Journal of Trace Elements in Medicine and Biology. 2014, 28(3), 247-254. DOI: https://doi.org/10.1016/j.jtemb.2014.03.005. ISSN 0946-672X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0946672X14000467

[13] ROSNER, G., D. COENEN-STASS a H. KÖNIG. Environmental Health Criteria 125 [online]. Geneva: WHO, 1991 [cit. 2.9.2019]. Dostupné z: http://www.inchem.org/documents/ehc/ehc/ehc125.htm

[14] MELBER, Ch., D. KELLER a I MANGELSDORF. Environmental Health Criteria 226 [online]. First. Geneva: WHO, 2002 [cit. 2.9.2019]. Dostupné z: http://www.inchem.org/documents/ehc/ehc/ehc226.htm

[15] VYAS, Nitin, Andrew TURNER a Graham SEWELL. Platinum-based anticancer drugs in waste waters of a major UK hospital and predicted concentrations in recipient surface waters. Science of The Total Environment. 2014, 493, 324-329. DOI: https://doi.org/10.1016/j.scitotenv.2014.05.127. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969714008195

[16] TURNER, Andrew a Llucia MASCORDA. Particle–water interactions of platinum-based anticancer drugs in river water and estuarine water. Chemosphere. 2015, 119, 415-422. DOI: https://doi.org/10.1016/j.chemosphere.2014.06.074. ISSN 0045-6535. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0045653514008212

[17] GAROUFIS, A., S.K. HADJIKAKOU a N. HADJILIADIS. Palladium coordination compounds as anti-viral, anti-fungal, anti-microbial and anti-tumor agents. Coordination Chemistry Reviews. 2009, 253(9), 1384-1397. DOI: https://doi.org/10.1016/j.ccr.2008.09.011. ISSN 0010-8545. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0010854508001744

[18] MAVROIDI, Barbara, Marina SAGNOU, Kostas STAMATAKIS, Maria PARAVATOU-PETSOTAS, Maria PELECANOU a Constantinos METHENITIS. Palladium(II) and platinum(II) complexes of derivatives of 2-(4′-aminophenyl)benzothiazole as potential anticancer agents. Inorganica Chimica Acta. 2016, 444, 63-75. DOI: https://doi.org/10.1016/j.ica.2016.01.012. ISSN 0020-1693. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0020169316000232

[19] LENZ, Katharina, Gunda KOELLENSPERGER, Stephan HANN, Norbert WEISSENBACHER, Susanne MAHNIK a Maria FUERHACKER. Fate of cancerostatic platinum compounds in biological wastewater treatment of hospital effluents. Chemosphere. 2007, 69(11), 1765-1774. DOI: https://doi.org/10.1016/j.chemosphere.2007.05.062. ISSN 0045-6535. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0045653507007199

[20] MASHIO, Asami, Hajime OBATA, Hirofumi TAZOE, Makoto TSUTSUMI, Antoni FERRER I SANTOS a Toshitaka GAMO. Dissolved platinum in rainwater, river water and seawater around Tokyo Bay and Otsuchi Bay in Japan. Estuarine, Coastal and Shelf Science. 2016, 180, 160-167. DOI: https://doi.org/10.1016/j.ecss.2016.07.002. ISSN 0272-7714. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0272771416302189

[21] CHEN, Mingliang, Sangxia CHEN, Mi DU et al. Toxic effect of palladium on embryonic development of zebrafish. Aquatic Toxicology. 2015, 159, 208-216. DOI: https://doi.org/10.1016/j.aquatox.2014.12.015. ISSN 0166-445X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0166445X14003889

[22] ZIMMERMANN, Sonja, Carolina WOLFF a Bernd SURES. Toxicity of platinum, palladium and rhodium to Daphnia magna in single and binary metal exposure experiments. Environmental Pollution. 2017, 224, 368-376. DOI: https://doi.org/10.1016/j.envpol.2017.02.016. ISSN 0269-7491. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0269749116326550

[23] KOSAROVA, Hedvika, Renata KOMENDOVA a Robert SKERIL. DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF PLATINUM IN URBAN DUST IN THE AGGLOMERATION OF BRNO, CZECH REPUBLIC. Fresenius Environmental Bulletin. 2015, 24(6), 2070-2075. ISSN 1018-4619. Dostupné také z: Go to ISI://WOS:000371185200010

[24] RINKOVEC, Jasmina, Gordana PEHNEC, Ranka GODEC, Silvije DAVILA a Ivan BEŠLIć. Spatial and temporal distribution of platinum, palladium and rhodium in Zagreb air. Science of The Total Environment. 2018, 636, 456-463. DOI: https://doi.org/10.1016/j.scitotenv.2018.04.295. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969718314736

[25] KOMENDOVA, R. a S. JEZEK. The distribution of platinum in the environment in large cities: a model study from Brno, Czech Republic. International Journal of Environmental Science and Technology. 2019, (16), 3109-3116. DOI: 10.1007/s13762-018-1954-x. ISSN 1735-1472. Dostupné také z: http://link.springer.com/10.1007/s13762-018-1954-x

[26] ORECCHIO, Santino a Diana AMORELLO. Platinum levels in urban soils from Palermo (Italy); Analytical method using voltammetry. Microchemical Journal. 2011, 99(2), 283-288. DOI: https://doi.org/10.1016/j.microc.2011.05.016. ISSN 0026-265X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0026265X11001081

[27] BIRKE, Manfred, Uwe RAUCH, Jens STUMMEYER, Hans LORENZ a Beate KEILERT. A review of platinum group element (PGE) geochemistry and a study of the changes of PGE contents in the topsoil of Berlin, Germany, between 1992 and 2013. Journal of Geochemical Exploration. 2018, 187, 72-96. DOI: https://doi.org/10.1016/j.gexplo.2017.09.005. ISSN 0375-6742. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0375674217306374

[28] KOMENDOVA, R. The use of bioindicators for assessing atmospheric pollution with platinum metals. Fresenius Environ Bull. 2018, 5, 3444-3451.

[29] GAWROńSKA, Helena, Arkadiusz PRZYBYSZ, Elżbieta SZALACHA, Katarzyna PAWLAK, Katarzyna BRAMA, Agata MISZCZAK, Marta STANKIEWICZ-KOSYL a Stanisław GAWROńSKI. Platinum uptake,

distribution and toxicity in Arabidopsis thaliana L. plants. Ecotoxicology and Environmental Safety. 2018, 147, 982-989. DOI: https://doi.org/10.1016/j.ecoenv.2017.09.065. ISSN 0147-6513. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0147651317306632

[30] KÜMMERER, Klaus, Eckard HELMERS, Peter HUBNER, Georges MASCART, Milena MILANDRI, Franz REINTHALER a Mirriam ZWAKENBERG. European hospitals as a source for platinum in the environment in comparison with other sources. Science of The Total Environment. 1999, 225(1), 155-165. DOI: https://doi.org/10.1016/S0048-9697(98)00341-6. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969798003416

[31] NOVOTNÝ, Matěj. Studium kontaminace říčních sedimentů platinovými kovy. Brno, 2018. Diplomová práce. Vysoké učení technické v Brně, Fakulta chemická. Vedoucí práce Renata Komendová.

[32] ABDOU, Melina, Jörg SCHÄFER, Ruoyu HU et al. Platinum in sediments and mussels from the northwestern Mediterranean coast: Temporal and spatial aspects: Temporal and spatial aspects. Chemosphere. 2019, 215, 783-792. DOI: https://doi.org/10.1016/j.chemosphere.2018.10.011. ISSN 0045-6535. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0045653518318599

[33] EK, Kristine, Sebastien RAUCH, Gregory MORRISON a Peter LINDBERG. Platinum group elements in raptor eggs, faeces, blood, liver and kidney. Science of The Total Environment. 2004, 334-335, 149-159. DOI: https://doi.org/10.1016/j.scitotenv.2004.04.067. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969704003699

[34] WANG, Yajun a Xiaozheng LI. Health Risk of Platinum Group Elements from Automobile Catalysts. Procedia Engineering. 2012, 45, 1004-1009. DOI: https://doi.org/10.1016/j.proeng.2012.08.273. ISSN 1877-7058. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S1877705812032857

[35] MUNKER, Sven, Sonja KILO, Christoph RÖß, Peter JEITNER, Rudolf SCHIERL, Thomas GÖEN a Hans DREXLER. Exposure of the German general population to platinum and rhodium − Urinary levels and determining factors. International Journal of Hygiene and Environmental Health. 2016, 219(8), 801-810. DOI: https://doi.org/10.1016/j.ijheh.2016.07.019. ISSN 1438-4639. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S143846391630061X

[36] RAO, C.R.M a G.S REDDI. Platinum group metals (PGM); occurrence, use and recent trends in their determination. TrAC Trends in Analytical Chemistry. 2000, 19(9), 565-586. DOI: https://doi.org/10.1016/S0165-9936(00)00031-5. ISSN 0165-9936. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0165993600000315

[37] THOMAS, Robert. Practical Guide to ICP-MS [online]. 1. New York: CRC Press, 2008 [cit. 2019-10-17]. ISBN 0-8247-5319-4. Dostupné z: http://algol.fis.uc.pt/jap/ICP-MS-Primer-Thomas.pdf

[38] CAMEL, Valérie. Solid-phase extraction. Sample Preparation for Trace Element Analysis. Elsevier, 2003, 41, s. 393-457. DOI: https://doi.org/10.1016/S0166-526X(03)41014-3. ISSN 0166-526X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0166526X03410143

[39] CAMEL, Valérie. Solid phase extraction of trace elements. Spectrochimica Acta Part B: Atomic Spectroscopy. 2003, 58(7), 1177-1233. DOI: https://doi.org/10.1016/S0584-8547(03)00072-7. ISSN 0584-8547. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0584854703000727

[40] MARCINKOWSKA, Renata, Karolina KONIECZNA, Łukasz MARCINKOWSKI, Jacek NAMIEśNIK a Adam KLOSKOWSKI. Application of ionic liquids in microextraction techniques: Current trends and future perspectives: Current trends and future perspectives. TrAC Trends in Analytical Chemistry. 2019, 119, 115614. DOI: https://doi.org/10.1016/j.trac.2019.07.025. ISSN 0165-9936. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S016599361930175X

[41] YIN, Xiaolu, Huilin YI, Qi WANG, Yudong WANG, Xu SUN, Cheng LV, Jinxin GUO a Yanzhao YANG. Extraction and separation of multiple platinum group metals from hydrochloric acid solution with sole 1-hexyl-3-methylimidazole-2-thione using microextraction method. Hydrometallurgy. 2017, 174, 167-174. DOI: https://doi.org/10.1016/j.hydromet.2017.10.009. ISSN 0304-386X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0304386X17304899

[42] TONG, Y., C. WANG, Y. HUANG a Y. YANG. Extraction and stripping of platinum from hydrochloric acid medium by mixed imidazolium ionic liquids. Industrial and Engineering Chemistry Research. 2015, 54(2), 705-711. DOI: 10.1021/ie503502g. Dostupné také z: https://www.scopus.com/inward/record.uri?eid=2-s2.0-84921690304&doi=10.1021%2fie503502g&partnerID=40&md5=b115d2fb2dc30ad356f179df67e86ee9

[43] VLASANKOVA, R a L SOMMER. Solid phase extraction and preconcentration for the determination of trace amounts of platinum group metals in environmental and biotic material - A critical review. Chemical Papers-Chemicke Zvesti. 1999, 53(3), 200-209. ISSN 0366-6352.

[44] LEE, M.L., G. TÖLG, E. BEINROHR a P. TSCHÖPEL. Preconcentration of palladium, platinum and rhodium by on-line sorbent extraction for graphite furnace atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry. Analytica Chimica Acta. 1993, 272(2), 193-203. DOI: https://doi.org/10.1016/0003-2670(93)80569-7. ISSN 0003-2670. Dostupné také z: http://www.sciencedirect.com/science/article/pii/0003267093805697

[45] VLAŠÁNKOVÁ, Renata. Extrakce mikrokoncentrací platinových kovů a zlata do pevných sorbentů a jejich stanovení metodou ICP-AES v objektech životního prostředí. Brno, 2001. Disertační práce. VUT v Brně, Fakulta chemická. Vedoucí práce Lumír Sommer.

[46] MUZIKAR, M., C. FONTàS, M. HIDALGO, J. HAVEL a V. SALVADÓ. A preconcentration system using polyamine Metalfix-Chelamine resin for the on-line determination of palladium(II) and platinum(IV) by inductively coupled plasma optical emission spectrometry. Talanta. 2006, 70(5), 1081-1086. DOI: https://doi.org/10.1016/j.talanta.2006.02.021. ISSN 0039-9140. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0039914006001494

[47] MORCALI, Mehmet a Bihter ZEYTUNCU. Investigation of adsorption parameters for platinum and palladium onto a modified polyacrylonitrile-based sorbent. International Journal of Mineral Processing. 2015, 137, 52-58. DOI:

https://doi.org/10.1016/j.minpro.2015.02.011. ISSN 0301-7516. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0301751615000277

[48] KOMENDOVA, R., J. NEVRLA, J. KUTA a L. SOMMER. INNOVATIVE PRECONCENTRATION TECHNIQUE ON POLYMER SORBENT FOR SIMULTANEOUS DETERMINATION OF PLATINUM GROUP METALS IN THE WATERS AND LICHEN HYPOGYMNIA PHYSODES. Fresenius Environmental Bulletin. 2016, 25(12), 5172-5179. ISSN 1018-4619. Dostupné také z: Go to ISI://WOS:000391345600011

[49] BARUA, Suman, Ismail RAHMAN, Maho MIYAGUCHI, Asami MASHIO, Teruya MAKI a Hiroshi HASEGAWA. On-site analysis of gold, palladium, or platinum in acidic aqueous matrix using liquid electrode plasma-optical emission spectrometry combined with ion-selective preconcentration. Sensors and Actuators B: Chemical. 2018, 272, 91-99. DOI: https://doi.org/10.1016/j.snb.2018.05.132. ISSN 0925-4005. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0925400518310414

[50] VLASANKOVA, R, V OTRUBA, J BENDL, M FISERA a V KANICKY. Preconcentration of platinum group metals on modified silicagel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates. Talanta. 1999, 48(4), 839-846. DOI: 10.1016/S0039-9140(98)00100-3. ISSN 0039-9140.

[51] KOMENDOVA-VLASANKOVA, R a L SOMMER. Separation and preconcentration of platinum group metals and gold on modified silica and XAD sorbents in the presence of cationic surfactants for their determination by ICP-AES. Collection of Czechoslovak Chemical Communications. 2002, 67(4), 454-470. DOI: 10.1135/cccc20020454. ISSN 0010-0765.

[52] BOSCH OJEDA, C, F SÁNCHEZ ROJAS, J.M CANO PAVÓN a A GARCíA DE TORRES. Automated on-line separation–preconcentration system for platinum determination by electrothermal atomic absorption spectrometry. Analytica Chimica Acta. 2003, 494(1), 97-103. DOI: https://doi.org/10.1016/S0003-2670(03)01014-6. ISSN 0003-2670. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0003267003010146

[53] TOKALıOğLU, Şerife, Tülay OYMAK a Şenol KARTAL. Determination of palladium in various samples by atomic absorption spectrometry after preconcentration with dimethylglyoxime on silica gel. Analytica Chimica Acta. 2004, 511(2), 255-260. DOI: https://doi.org/10.1016/j.aca.2004.02.015. ISSN 0003-2670. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0003267004001928

[54] WU, X.Z, P LIU, Q.S PU, Q.Y SUN a Z.X SU. Preparation of dendrimer-like polyamidoamine immobilized silica gel and its application to online preconcentration and separation palladium prior to FAAS determination. Talanta. 2004, 62(5), 918-923. DOI: https://doi.org/10.1016/j.talanta.2003.10.011. ISSN 0039-9140. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0039914003005952

[55] ROJAS, F., C. OJEDA a J.M. PAVÓN. Automated on-line separation preconcentration system for palladium determination by graphite furnace atomic absorption spectrometry and its application to palladium determination in environmental and food samples. Talanta. 2006, 70(5), 979-983. DOI: https://doi.org/10.1016/j.talanta.2006.05.048. ISSN 0039-9140. Dostupné také z:

http://www.sciencedirect.com/science/article/pii/S0039914006003754

[56] SHARMA, R.K., Amit PANDEY, Shikha GULATI a Alok ADHOLEYA. An optimized procedure for preconcentration, determination and on-line recovery of palladium using highly selective diphenyldiketone-monothiosemicarbazone modified silica gel. Journal of Hazardous Materials. 2012, 209-210, 285-292. DOI: https://doi.org/10.1016/j.jhazmat.2012.01.022. ISSN 0304-3894. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0304389412000519

[57] NISCHKAUER, Winfried, Marie-Alexandra NEOUZE, Frank VANHAECKE a Andreas LIMBECK. Extraction and pre-concentration of platinum and palladium from microwave-digested road dust via ion exchanging mesoporous silica microparticles prior to their quantification by quadrupole ICP-MS. Mikrochimica acta. Springer Vienna, 2015, 182(15-16), 2369-2376. DOI: 10.1007/s00604-015-1643-0. ISSN 0026-3672. Dostupné také z: https://www.ncbi.nlm.nih.gov/pubmed/26500376

[58] BARCZAK, Mariusz, Joanna DOBRZYńSKA, Monika OSZUST, Ewa SKWAREK, Jarosław OSTROWSKI, Emil ZIęBA, Piotr BOROWSKI a Ryszard DOBROWOLSKI. Synthesis and application of thiolated mesoporous silicas for sorption, preconcentration and determination of platinum. Materials Chemistry and Physics. 2016, 181, 126-135. DOI: https://doi.org/10.1016/j.matchemphys.2016.06.042. ISSN 0254-0584. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0254058416304564

[59] DOBRZYńSKA, J., R. DOBROWOLSKI, R. OLCHOWSKI, E. ZIęBA a M. BARCZAK. Palladium adsorption and preconcentration onto thiol- and amine-functionalized mesoporous silicas with respect to analytical applications. Microporous and Mesoporous Materials. 2019, 274, 127-137. DOI: https://doi.org/10.1016/j.micromeso.2018.07.038. ISSN 1387-1811. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S138718111830413X

[60] KOMENDOVA, Renata. The HR-CS-GF-AAS determination and preconcentration of palladium in contaminated urban areas, especially in lichens. Environmental Pollution. 2020, 256, 113468. DOI: https://doi.org/10.1016/j.envpol.2019.113468. ISSN 0269-7491. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0269749119331173

[61] GAITA, Romulus a Sargon AL-BAZI. An ion-exchange method for selective separation of palladium, platinum and rhodium from solutions obtained by leaching automotive catalytic converters. Talanta. 1995, 42(2), 249-255. DOI: https://doi.org/10.1016/0039-9140(94)00246-O. ISSN 0039-9140. Dostupné také z: http://www.sciencedirect.com/science/article/pii/003991409400246O

[62] JARVIS, Ian, Marina TOTLAND a Kym JARVIS. Assessment of Dowex 1-X8-based Anion-exchange Procedures for the Separation and Determination of Ruthenium, Rhodium, Palladium, Iridium, Platinum and Gold in Geological Samples by Inductively Coupled Plasma Mass Spectrometry. The Analyst. 1997, 122(1), 19-26. DOI: 10.1039/a606169i. ISSN 00032654. Dostupné také z: http://xlink.rsc.org/?DOI=a606169i

[63] KOVACHEVA, Petya a Rumyana DJINGOVA. Ion-exchange method for separation and concentration of platinum and palladium for analysis of environmental samples by inductively coupled plasma atomic emission spectrometry. Analytica Chimica Acta. 2002, 464(1), 7-13. DOI: https://doi.org/10.1016/S0003-2670(02)00428-2. ISSN 0003-2670. Dostupné také

z: http://www.sciencedirect.com/science/article/pii/S0003267002004282

[64] GONZÁLEZ GARCÍA, M., F. SÁNCHEZ ROJAS, C. BOSCH OJEDA, A. GARCÍA DE TORRES a J. CANO PAVÓN. On-line ion-exchange preconcentration and determination of traces of platinum by electrothermal atomic absorption spectrometry. Analytical and Bioanalytical Chemistry. 2003, 375(8), 1229-1233. DOI: 10.1007/s00216-002-1679-y. ISSN 1618-2650. Dostupné také z: https://doi.org/10.1007/s00216-002-1679-y

[65] MARTOS, N., P. RUDNER, A. DE TORRES a J. PAVÓN. Development of an FI-ICP Method for On-Line Preconcentration and Determination of Platinum. Microchimica Acta. 2004, 148(1), 35-42. DOI: 10.1007/s00604-004-0256-9. ISSN 1436-5073. Dostupné také z: https://doi.org/10.1007/s00604-004-0256-9

[66] SUN, P.P., J.Y. LEE a M.S. LEE. Separation of platinum(IV) and rhodium(III) from acidic chloride solution by ion exchange with anion resins. Hydrometallurgy. 2012, 113-114, 200-204. DOI: https://doi.org/10.1016/j.hydromet.2011.12.009. ISSN 0304-386X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0304386X11002623

[67] ALONSO CASTILLO, Manuel, Amparo GARCÍA DE TORRES, Elisa VEREDA ALONSO, M SILES CORDERO a José CANO PAVÓN. Multi-element determination of Pt, Pd and Ir traces in environmental samples by ICP-MS after pre-concentration. Talanta. 2012, 99, 853-858. DOI: https://doi.org/10.1016/j.talanta.2012.07.042. ISSN 0039-9140. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0039914012006182

[68] NIKOLOSKI, Aleksandar, Kwang-Loon ANG a Dan LI. Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins. Hydrometallurgy. 2015, 152, 20-32. DOI: https://doi.org/10.1016/j.hydromet.2014.12.006. ISSN 0304-386X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0304386X14002783

[69] MIROSHNICHENKO, A.A. Sorption Recovery of Platinum Metals from Compound Solutions. Procedia Engineering. 2016, 152, 8-12. DOI: https://doi.org/10.1016/j.proeng.2016.07.607. ISSN 1877-7058. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S187770581632015X

[70] JEŽEK, Stanislav. STANOVENÍ PLATINOVÝCH KOVŮ VE VELKÝCH MĚSTSKÝCH AGLOMERACÍCH. Brno, 2016. Diplomová práce. Vysoké učení technické v Brně, Fakulta Chemická. Vedoucí práce Renata Komendová.

[71] SÝKORA, Jiří. Využití iontoměničů pro prekoncentraci platinových kovů. Brno, 2017. Diplomová práce. Vysoké učení technické v Brně, Fakulta chemická. Vedoucí práce Renata Komendová.

[72] JARVIS, Ian, Marina TOTLAND a Kym JARVIS. Determination of the platinum-group elements in geological materials by ICP-MS using microwave digestion, alkali fusion and cation-exchange chromatography. Chemical Geology. 1997, 143(1), 27-42. DOI: https://doi.org/10.1016/S0009-2541(97)00098-3. ISSN 0009-2541. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0009254197000983

[73] WHITELEY, J.D a F MURRAY. Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. Science of The Total Environment. 2003, 317(1), 121-135. DOI: https://doi.org/10.1016/S0048-9697(03)00359-0. ISSN 0048-9697. Dostupné také

z: http://www.sciencedirect.com/science/article/pii/S0048969703003590

[74] WHITELEY, J.D. a F. MURRAY. Autocatalyst-derived platinum, palladium and rhodium (PGE) in infiltration basin and wetland sediments receiving urban runoff. Science of The Total Environment. 2005, 341(1), 199-209. DOI: https://doi.org/10.1016/j.scitotenv.2004.09.030. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969704006710

[75] AFZALI, Daryoush, Rasool JAMSHIDI, Sima GHASEMINEZHAD a Zahra AFZALI. Preconcentration procedure trace amounts of palladium using modified multiwalled carbon nanotubes sorbent prior to flame atomic absorption spectrometry: 1st Nano Update: 1st Nano Update. Arabian Journal of Chemistry. 2012, 5(4), 461-466. DOI: https://doi.org/10.1016/j.arabjc.2011.01.017. ISSN 1878-5352. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S1878535211000219

[76] TAHER, Mohammad, Zahra DALIRI a Hamid FAZELIRAD. Simultaneous extraction and preconcentration of copper, silver and palladium with modified alumina and their determination by electrothermal atomic absorption spectrometry. Chinese Chemical Letters. 2014, 25(4), 649-654. DOI: https://doi.org/10.1016/j.cclet.2013.12.025. ISSN 1001-8417. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S100184171400059X

[77] HONG, Hye-Jin, Hayoung YU, Minsang PARK a Hyeon JEONG. Recovery of platinum from waste effluent using polyethyleneimine-modified nanocelluloses: Effects of the cellulose source and type: Effects of the cellulose source and type. Carbohydrate Polymers. 2019, 210, 167-174. DOI: https://doi.org/10.1016/j.carbpol.2019.01.079. ISSN 0144-8617. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S014486171930092X

[78] SOMMER, L a R VLASANKOVA. A survey of the potential of the high performance liquid chromatography and capillary zone electrophoresis for the determination of platinum and platinum group metals. Chromatographia. 2000, 52(11-12), 692-702. DOI: 10.1007/BF02490992. ISSN 0009-5893.

[79] NAKAJIMA, Junichi, Masashi OHNO, Katsumi CHIKAMA, Tatsuya SEKI a Koichi OGUMA. Determination of traces of palladium in stream sediment and auto catalyst by FI-ICP-OES using on-line separation and preconcentration with QuadraSil TA. Talanta. 2009, 79(4), 1050-1054. DOI: https://doi.org/10.1016/j.talanta.2009.02.035. ISSN 0039-9140. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0039914009001672

[80] KOMENDOVA, Renata. Recent advances in the preconcentration and determination of platinum group metals in environmental and biological samples. TrAC Trends in Analytical Chemistry. 2020, 122, 115708. DOI: https://doi.org/10.1016/j.trac.2019.115708. ISSN 0165-9936. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0165993619304741

[81] WISEMAN, Clare, Fathi ZEREINI, ed. Platinum Metals in the Environment. 1. Berlin: Springer, 2015. ISBN 978-3-662-44559-4.

[82] Cisplatina. Www.sukl.cz [online]. [cit. 2019-07-24].

[83] ŠEBEK, O., M. MIHALJEVIČ, L. STRNAD et al. Dissolution kinetics of Pd and Pt from automobile catalysts by naturally occurring complexing agents. Journal of Hazardous Materials. 2011, 198, 331-339. DOI: 10.1016/j.jhazmat.2011.10.051. Dostupné také z: https://www.scopus.com/inward/record.uri?eid=2-s2.0-

82955201817&doi=10.1016%2fj.jhazmat.2011.10.051&partnerID=40&md5=bf1c263017a10eade4550c4324e02cf3

[84] ZEREINI, Fathi, ed. a Friedrich ALT, ed. Palladium Emissions in the Environment. 1. Berlin: Springer, 2005. ISBN 978-3-540-29219-7.

[85] ANDĚL, Petr. Ekotoxikologie, bioindikace a biomonitoring. 1. Liberec, 2011. ISBN 978-80-903787-9-7.

[86] VLAŠÁNKOVÁ, Renata. Prekoncentrace platinových kovů pro stanovení plazmovou spektrometrií ve vzorcích z životního prostředí. Brno, 1997. Diplomová práce. Masarykova univerzita v Brně, Přírodovědecká fakulta. Vedoucí práce Viktor Kanický.

[87] SCHIERL, Rudi. Environmental monitoring of platinum in air and urine. Microchemical Journal. 2000, 67(1), 245-248. DOI: https://doi.org/10.1016/S0026-265X(00)00068-0. ISSN 0026-265X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0026265X00000680

[88] VAŠÁTKO, Jan. Aplikace elektrochemických metod pro stanovení platinových kovů. Brno, 2017. Bakalářská práce. Vysoké učení technické v Brně, Fakulta chemická. Vedoucí práce Renata Komendová.

[89] SHARMA, Mukul. Platinum Group Elements and Their Isotopes in the Ocean. Oxford: Academic Press, 2019, s. 174-180. DOI: https://doi.org/10.1016/B978-0-12-409548-9.11556-8. ISBN 978-0-12-813082-7. Dostupné také z: http://www.sciencedirect.com/science/article/pii/B9780124095489115568

[90] LÓPEZ-SÁNCHEZ, Daniel, Antonio COBELO-GARCÍA, Micha RIJKENBERG, Loes GERRINGA a Hein DE BAAR. New insights on the dissolved platinum behavior in the Atlantic Ocean. Chemical Geology. 2019, 511, 204-211. DOI: https://doi.org/10.1016/j.chemgeo.2019.01.003. ISSN 0009-2541. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0009254119300038

[91] COBELO-GARCÍA, Antonio, Patricia NEIRA, Mario MIL-HOMENS a Miguel CAETANO. Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal). Marine Pollution Bulletin. 2011, 62(3), 646-650. DOI: https://doi.org/10.1016/j.marpolbul.2010.12.018. ISSN 0025-326X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0025326X10005412

[92] ABDOU, M., J. SCHÄFER, A. COBELO-GARCÍA, P. NEIRA, J.C.J. PETIT, D. AUGER, J.-F. CHIFFOLEAU a G. BLANC. Past and present platinum contamination of a major European fluvial–estuarine system: Insights from river sediments and estuarine oysters: Insights from river sediments and estuarine oysters. Marine Chemistry. 2016, 185, 104-110. DOI: https://doi.org/10.1016/j.marchem.2016.01.006. ISSN 0304-4203. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0304420316300068

[93] PAVLÍČKOVÁ, Ivana. Stanovení platinových kovů v půdách na území města Brna. Brno, 2015. Diplomová práce. Vysoké učení technické v Brně, Fakulta chemická. Vedoucí práce Renata Komendová.

[94] WISEMAN, Clare, Zahra HASSAN POUR a Fathi ZEREINI. Platinum group element and cerium concentrations in roadside environments in Toronto, Canada. Chemosphere. 2016, 145, 61-67. DOI: https://doi.org/10.1016/j.chemosphere.2015.11.056. ISSN 0045-6535. Dostupné

také z: http://www.sciencedirect.com/science/article/pii/S0045653515303908

[95] RENTSCHLER, Gerda, Ilia RODUSHKIN, Milena CERNA et al. Platinum, palladium, rhodium, molybdenum and strontium in blood of urban women in nine countries. International Journal of Hygiene and Environmental Health. 2018, 221(2), 223-230. DOI: https://doi.org/10.1016/j.ijheh.2017.10.017. ISSN 1438-4639. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S1438463917304042

[96] GONCALVES, Antonio, José DOMÍNGUEZ a José ALVARADO. Determination of Pd, Pt and Rh in vehicles escape fumes by GF-AAS and ICP-OES. Talanta. 2008, 75(2), 523-527. DOI: https://doi.org/10.1016/j.talanta.2007.11.055. ISSN 0039-9140. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0039914007008065

[97] PAUKERT, Tomáš a Ivan RUBEŠKA. Effects of fusion charge composition on the determination of platinum group elements using collection into a minimized nickel sulphide button. Analytica Chimica Acta. 1993, 278(1), 125-136. DOI: https://doi.org/10.1016/0003-2670(93)80091-X. ISSN 0003-2670. Dostupné také z: http://www.sciencedirect.com/science/article/pii/000326709380091X

[98] COLOMBO, Claudia, A. MONHEMIUS a Jane PLANT. The estimation of the bioavailabilities of platinum, palladium and rhodium in vehicle exhaust catalysts and road dusts using a physiologically based extraction test. Science of The Total Environment. 2008, 389(1), 46-51. DOI: https://doi.org/10.1016/j.scitotenv.2007.08.022. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969707008765

[99] NAVROTSKY, Alexandra. Materials and nanotechnology. Journal of the Franklin Institute. 2003, 340(3), 263-268. DOI: https://doi.org/10.1016/S0016-0032(03)00044-9. ISSN 0016-0032. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0016003203000449

[100] ELDER, A., H. YANG, R. GWIAZDA, X. TENG, S. THURSTON, H. HE a G. OBERDÖRSTER. Testing Nanomaterials of Unknown Toxicity: An Example Based on Platinum Nanoparticles of Different Shapes: An Example Based on Platinum Nanoparticles of Different Shapes. Advanced Materials. John Wiley & Sons, Ltd, 2007, 19(20), 3124-3129. DOI: 10.1002/adma.200701962. ISSN 0935-9648. Dostupné také z: https://doi.org/10.1002/adma.200701962

[101] RÜHLE, T., H. SCHNEIDER, J. FIND et al. Preparation and characterisation ofPt/Al2O3 aerosol precursors as model Pt-emissions from catalytic converters. Applied Catalysis B: Environmental. 1997, 14(1), 69-84. DOI: https://doi.org/10.1016/S0926-3373(97)00013-1. ISSN 0926-3373. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0926337397000131

[102] PRICHARD, Hazel a Peter FISHER. Identification of platinum and palladium particles emitted from vehicles and dispersed into the surface environment. Environmental Science and Technology. 2012, 46(6), 3149-3154.

[103] FOLENS, Karel, Thibaut VAN ACKER, Eduardo BOLEA-FERNANDEZ, Geert CORNELIS, Frank VANHAECKE, Gijs DU LAING a Sebastien RAUCH. Identification of platinum nanoparticles in road dust leachate by single particle inductively coupled plasma-mass spectrometry. Science of The Total Environment. 2018, 615, 849-856. DOI: https://doi.org/10.1016/j.scitotenv.2017.09.285. ISSN 0048-9697. Dostupné také

z: http://www.sciencedirect.com/science/article/pii/S0048969717326360

[104] ASHARANI, P.V., Y. LIANWU, Z. GONG a S. VALIYAVEETTIL. Comparison of the toxicity of silver, gold and platinum nanoparticles in developing zebrafish embryos. Nanotoxicology. 2011, 5(1), 43-54. DOI: 10.3109/17435390.2010.489207. Dostupné také z: https://www.scopus.com/inward/record.uri?eid=2-s2.0-79952838115&doi=10.3109%2f17435390.2010.489207&partnerID=40&md5=e4ac6a57644637b8ddcc86508bac4b62

[105] KSIąZYK, M., M. ASZTEMBORSKA, R. STęBOROWSKI a G. BYSTRZEJEWSKA-PIOTROWSKA. Toxic effect of silver and platinum nanoparticles toward the freshwater microalga Pseudokirchneriella subcapitata. Bulletin of Environmental Contamination and Toxicology. 2015, 94(5), 554-558. DOI: 10.1007/s00128-015-1505-9. Dostupné také z: https://www.scopus.com/inward/record.uri?eid=2-s2.0-84939963025&doi=10.1007%2fs00128-015-1505-9&partnerID=40&md5=d01dc4ddd6ddfe96910b92c69036a75f

[106] DEPCIUCH, J., M. STEC, B. KLEBOWSKI, A. MAXIMIENKO, E. DRZYMAłA, J. BARAN a M. PARLINSKA-WOJTAN. Size effect of platinum nanoparticles in simulated anticancer photothermal therapy. Photodiagnosis and Photodynamic Therapy. 2019, , 101594. DOI: https://doi.org/10.1016/j.pdpdt.2019.101594. ISSN 1572-1000. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S1572100019305290

[107] GAO, J., G. LIANG, B. ZHANG, Y. KUANG, X. ZHANG a B. XU. FePt@CoS2 yolk-shell nanocrystals as a potent agent to kill HeLa cells. Journal of the American Chemical Society. 2007, 129(5), 1428-1433. DOI: 10.1021/ja067785e. Dostupné také z: https://www.scopus.com/inward/record.uri?eid=2-s2.0-33846813692&doi=10.1021%2fja067785e&partnerID=40&md5=4b6845f0121941c72bfc49222c2dfe9b

[108] BUNDSCHUH, Mirco, Juliane FILSER, Simon LÜDERWALD, Moira MCKEE, George METREVELI, Gabriele SCHAUMANN, Ralf SCHULZ a Stephan WAGNER. Nanoparticles in the environment: where do we come from, where do we go to?: where do we come from, where do we go to?. Environmental sciences Europe. Springer Berlin Heidelberg, 2018, 30(1), 6-6. DOI: 10.1186/s12302-018-0132-6. ISSN 2190-4707. Dostupné také z: https://www.ncbi.nlm.nih.gov/pubmed/29456907

[109] BEHRA, R., B. WAGNER, L. SGIER a D. KISTLER. Colloidal Stability and Toxicity of Gold Nanoparticles and Gold Chloride on Chlamydomonas reinhardtii. Aquatic Geochemistry. 2015, 21(2-4), 331-342. DOI: 10.1007/s10498-015-9255-1. Dostupné také z: https://www.scopus.com/inward/record.uri?eid=2-s2.0-84931005942&doi=10.1007%2fs10498-015-9255-1&partnerID=40&md5=4831a39a9eae66221ff8d34b4dca7f0f

[110] TEJAMAYA, M., I. RÖMER, R.C. MERRIFIELD a J.R. LEAD. Stability of citrate, PVP, and PEG coated silver nanoparticles in ecotoxicology media. Environmental Science and Technology. 2012, 46(13), 7011-7017. DOI: 10.1021/es2038596. Dostupné také z: https://www.scopus.com/inward/record.uri?eid=2-s2.0-84863522464&doi=10.1021%2fes2038596&partnerID=40&md5=d70081e4f9be9

74db45a3e0ac63f8f5d

[111] SIKDER, Mithun, Jingjing WANG, G. CHANDLER, Debora BERTI a Mohammed BAALOUSHA. Synthesis, characterization, and environmental behaviors of monodispersed platinum nanoparticles. Journal of Colloid and Interface Science. 2019, 540, 330-341. DOI: https://doi.org/10.1016/j.jcis.2019.01.036. ISSN 0021-9797. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0021979719300505

[112] PUJA, Patel a Ponnuchamy KUMAR. A perspective on biogenic synthesis of platinum nanoparticles and their biomedical applications. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2019, 211, 94-99. DOI: https://doi.org/10.1016/j.saa.2018.11.047. ISSN 1386-1425. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S1386142518310448

[113] DOBRUCKA, Renata. Biofabrication of platinum nanoparticles using Fumariae herba extract and their catalytic properties. Saudi Journal of Biological Sciences. 2019, 26(1), 31-37. DOI: https://doi.org/10.1016/j.sjbs.2016.11.012. ISSN 1319-562X. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S1319562X16301693

[114] BISWAS, Pratim a Chang-Yu WU. Nanoparticles and the Environment. Journal of the Air & Waste Management Association (1995). 2005, 55, 708-46. DOI: 10.1080/10473289.2005.10464656.

[115] BUSECK, Peter a K. ADACHI. Nanoparticles in the Atmosphere. ELEMENTS. 2007, 4, 389-394. DOI: 10.2113/gselements.4.6.389.

[116] BUZEA, Cristina, Ivan PACHECO a Kevin ROBBIE. Nanomaterials and nanoparticles: Sources and toxicity: Sources and toxicity. Biointerphases. American Vacuum Society, 2007, 2(4), 17-71. DOI: 10.1116/1.2815690. ISSN 1934-8630. Dostupné také z: https://doi.org/10.1116/1.2815690

[117] THENG, Benny a G. YUAN. Nanoparticles in the Soil Environment. ELEMENTS. 2007, 4, 395-399. DOI: 10.2113/gselements.4.6.395.

[118] BAKSHI, Santanu, Zhenli HE a Willie HARRIS. Natural Nanoparticles: Implications for Environment and Human Health: Implications for Environment and Human Health. Critical Reviews in Environmental Science and Technology. 2014, 45. DOI: 10.1080/10643389.2014.921975.

[119] SHRIVASTAVA, Manoj, Akansha SRIVASTAV, Sonu GANDHI et al. Monitoring of engineered nanoparticles in soil-plant system: A review: A review. Environmental Nanotechnology, Monitoring & Management. 2019, 11, 100218. DOI: https://doi.org/10.1016/j.enmm.2019.100218. ISSN 2215-1532. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S2215153218303210

[120] KOMENDOVÁ, Renata, Jan ŽÍDEK, Michal BERKA, Marta JEMELKOVÁ, Veronika ŘEZÁČOVÁ, Pellegrino CONTE a Jiří KUČERÍK. Small-sized platinum nanoparticles in soil organic matter: Influence on water holding capacity, evaporation and structural rigidity: Influence on water holding capacity, evaporation and structural rigidity. Science of The Total Environment. 2019, 694, 133822. DOI: https://doi.org/10.1016/j.scitotenv.2019.133822. ISSN 0048-9697. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0048969719337696

[121] ZHANG, Hengzhong, Benjamin GILBERT, Feng HUANG a Jillian F. BANFIELD. Water-driven structure transformation in nanoparticles at room

temperature. Nature. 2003, 424(6952), 1025-1029. DOI: 10.1038/nature01845. ISSN 1476-4687. Dostupné také z: https://doi.org/10.1038/nature01845

[122] VOLKOV, R.S., G.V. KUZNETSOV a P.A. STRIZHAK. Experimental investigation of mixtures and foreign inclusions in water droplets influence on integral characteristics of their evaporation during motion through high-temperature gas area. International Journal of Thermal Sciences. 2015, 88, 193-200. DOI: https://doi.org/10.1016/j.ijthermalsci.2014.10.002. ISSN 1290-0729. Dostupné také z: http://www.sciencedirect.com/science/article/pii/S1290072914002865

[123] BOWLES, John a Andrew GIZE. A preliminary study of the release of platinum and palladium from metallic particles in the surface environment by organic acids: Relevance to weathering of particles from vehicle exhaust catalysts: Relevance to weathering of particles from vehicle exhaust catalysts. Mineralogical Magazine - MINER MAG. 2005, 69, 687-693. DOI: 10.1180/0026461056950280.

[124] RAJPUT, Vishnu, Tatiana MINKINA, Svetlana SUSHKOVA, Viktoriia TSITSUASHVILI, Saglara MANDZHIEVA, Andrey GOROVTSOV, Dina NEVIDOMSKYAYA a Natalya GROMAKOVA. Effect of Nanoparticles on Crops and Soil Microbial Communities. Journal of Soils and Sediments. 2017, , 2179–2187. DOI: 10.1007/s11368-017-1793-2.

9 SEZNAM PŘÍLOH

Příloha 1

VLASANKOVA, R. a L. SOMMER. Solid phase extraction and preconcentration for the determination of trace amounts of platinum group metals in environmental and biotic material - A critical review. *Chemical Papers-Chemicke Zvesti*. 1999a, **53**(3), 200-209. ISSN 0366-6352.

Příloha 2

SOMMER, L. a **R. VLASANKOVA**. A survey of the potential of the high performance liquid chromatography and capillary zone electrophoresis for the determination of platinum and platinum group metals. *Chromatographia*. 2000, **52**(11-12), 692-702. ISSN 0009-5893.
DOI: 10.1007/BF02490992.

Příloha 3

VLASANKOVA, R., V. OTRUBA, J. BENDL, M. FISERA a V. KANICKY. Preconcentration of platinum group metals on modified silicagel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates. *Talanta*. 1999b, **48**(4), 839-846. ISSN 0039-9140.
DOI: 10.1016/S0039-9140(98)00100-3.

Příloha 4

KOMENDOVA-VLASANKOVA, R. a L. SOMMER. Separation and preconcentration of platinum group metals and gold on modified silica and XAD sorbents in the presence of cationic surfactants for their determination by ICP-AES. *Collection of Czechoslovak Chemical Communications*. 2002, **67**(4), 454-470. ISSN 0010-0765.
DOI: 10.1135/cccc20020454.

Příloha 5

KOSAROVA, H., **KOMENDOVA R.*** a SKERIL R.. DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF PLATINUM IN URBAN DUST IN THE AGGLOMERATION OF BRNO, CZECH REPUBLIC. *Fresenius Environmental Bulletin*. 2015, **24**(6), 2070-2075. ISSN 1018-4619.
Dostupné také z: Go to ISI://WOS:000371185200010

Příloha 6

KOMENDOVA, R.* a JEZEK S.. The distribution of platinum in the environment in large cities: a model study from Brno, Czech Republic. *International Journal of Environmental Science and Technology*. 2019, **16**, 3109-3116. ISSN 1735-1472.
DOI: 10.1007/s13762-018-1954-x.
Dostupné také z: http://link.springer.com/10.1007/s13762-018-1954-x

Příloha 7

KOMENDOVA, R. The use of bioindicators for assessing atmospheric pollution with platinum metals. *Fresenius Environ Bull*. 2018, **5**, 3444-3451. ISSN 1018-4619.

Příloha 8

KOMENDOVA, R.*, J. NEVRLA, J. KUTA a L. SOMMER. INNOVATIVE PRECONCENTRATION TECHNIQUE ON POLYMER SORBENT FOR SIMULTANEOUS DETERMINATION OF PLATINUM GROUP METALS IN THE WATERS AND LICHEN HYPOGYMNIA PHYSODES. *Fresenius Environmental Bulletin*. 2016, **25**(12), 5172-5179. ISSN 1018-4619.
Dostupné také z: Go to ISI://WOS:000391345600011

Příloha 9

KOMENDOVA, R. The HR-CS-GF-AAS determination and preconcentration of palladium in contaminated urban areas, especially in lichens. *Environmental Pollution*. 2020, 256, 113468. DOI: https://doi.org/10.1016/j.envpol.2019.113468. ISSN 0269-7491.
Dostupné také z: http://www.sciencedirect.com/science/article/pii/S0269749119331173

Příloha 10

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REVIEW

Solid Phase Extraction and Preconcentration for the Determination of Trace Amounts of Platinum Group Metals in Environmental and Biotic Material
A Critical Review

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Approaches to preconcentration, separation, and determination of platinum group metals, especially platinum, in environmental and biotic material are reviewed and critically commented.

Nowadays a great attention is paid to the analytical chemistry of platinum group metals (PGM), especially platinum [1—3], for several deciding reasons.

a) A massive introduction of automobile catalytic converters on the basis of PGM (Pt, Pd, Rh) to remove toxic components of spark ignition engines. During this process microamounts of PGM are released into the exhaust and spread into the ambient air, airborn dust particles, road dust, soil and plants near to frequented highways and tunnels.

b) Several compounds of Pt(IV) and Pd(II) are nephrotoxic, gastrointestinal irritants and strong allergens already in ng-level against sensitized persons [4—6]. Pt(II) compounds may have mutagenic, genotoxic or carcinogenic properties. No comprehensive data about toxicity of other PGM are available till now.

c) Selected Pt(II) complex species are effective cytostatics being used in the therapy of some forms of cancer [7] and Pt(II) traces may appear on the equipment, in the rooms, ambient air or waste waters of some hospitals.

d) The need of determination of "ng- to subng-" levels of Pt and other PGM in environmental and biotic samples or when monitoring platinum in food chains. Several problems may appear when looking for certified reference materials or standards of environmental and biotic origin for extreme trace concentration range.

Abundance of Pt and Other PGM in the Environment or Body Fluids and their Determination

Detailed data for the environmental material and human body are available for platinum coming from the anthropogenic activity, *e.g.* in river and sea waters and their biotics [8—11], ambient air [8, 12, 13], airborn particles, road and tunnel dust [12, 14—17, 55, 56], plants near motorways [8, 18, 19], body fluids of exposed persons [12, 20—28]. The contents of Pd are usually considerably lower but may sometimes increase [8]. In the engine catalyst exhaust, platinum is mainly generated in elementary state and bound in the form of clusters to common metal oxide particles depending on the particle size [12, 14]. The heterogeneity with respect to Pt content in dust particles may cause serious incertainty and errors of analytical results for road dust, collected airborn dust particles, engine soot, and soil samples. A part of Pt is, however, in soluble state, penetrates into the soil and is uptaken by the plants growing around the motorways [18]. Soluble Pt can also be extracted from the road sediments [29].

When Pt is metabolized in plants, 90 % is bound to low-molecular species, such as methionine or dimethionine or peptide glutathione. The rest of platinum is fixed to high-molecular phytochelatines or to polygalacturonic acid behaving as ion exchanger [5, 18].

For monitoring the increase of platinum and other

PGM content in the environment and human body, the knowledge of the natural PGM background values is necessary. For their determination, extremely sensitive analytical methods are, however, necessary. Some average contents for platinum in rocky crust, sediments, sea waters, fresh air, biotics, and blood are mentioned in literature [4]. Some problems with their estimation are discussed by *Alt et al.* [30].

ET-AAS [19, 23, 31—33], ICP-AES [31, 32, 34—36], ICP-MS [19, 24, 37], adsorption voltamperometry [11, 21, 29, 38, 39], and neutron activation [13, 40] are considered as sensitive and selective methods for the determination of platinum and some other PGM in environmental and biotic matrices. The first three, however, are most easily applicable for the determination of "ng- and subng-" levels of platinum and other PGM in complicated matrices of the real world after separation and preconcentration of PGM.

For the ET-AAS in graphite cuvettes, detection limits ($3s_B$) among 0.5—6 μg dm^{-3} [41] or 3 μg dm^{-3} [42] are given for PGM in pure solutions depending on the conditions used. Drawbacks are coming from the little volatility of PGM and their tendency to form thermostable carbides, which requires a previous treatment of the cuvettes, platforms or the presence of modifiers. Common matrix elements interfere with the atomization process and must often be removed. The sensitivity and detection limits may be enhanced by slurry techniques [43, 44] or various kinds of preconcentrations or by the presence of oxygen in argon. High background levels especially for biotic samples and interferences from common metals and inert salts are observed [43].

ICP-AES of PGM in argon with determination limits 300—30 μg dm^{-3} [41] or 10.0—2.0 μg dm^{-3} [45] is less sensitive with classical nebulizers but advantageous because of little spectral interferences and broad linear calibration functions. Chemical interferences may be, however, serious in the presence of increased amounts of inert salts and common metal ions. Organic solvents of low polarity may also interfere.

ICP-MS is the most suitable method with the highest detection power and large dynamic concentration interval for PGM when internal standards or isotopic dilution [10] is used for quantitative evaluation. A variety of sample introduction modes into ICP, such as current or ultrasonic nebulization, thermospray nebulization, electrothermal vaporization [10, 25, 46—48], slurry technique in the presence of nonionic surfactants [46] or direct injection have been used. The method is, however, not free of serious limitation by matrix elements and components, mutual influence of PGM metals and acids in solution. This is often connected with the limited resolution of the attached mass spectrometer [41, 49]. Detection limits of PGM for pure solutions have been compared for ET-AAS, ICP-AES, and ICP-MS [41].

The application of on-line flow systems with hyphenated techniques containing separation columns is often hindered by the slow kinetics in connection with the formation of PGM chelates or ion associates during the separation and preconcentration or has some drawbacks if microvolumes are sampled in the ET-AAS.

Values for the platinum content in the environment obtained by ET-AAS and ICP-MS from several laboratories were tested with respect of the rules of quality assurance and quality control including sampling and sample decomposition. Considerable differences have been observed among the results [50].

HPLC may be used with advantage for the separation and evaluation of low-molecular platinum species in biotic and soil samples [51]. A hyphenated combination of HPLC-ICP-MS is readily suitable when hydrophobic derivatized silica gel, the gradient elution on the basis of CH_3CN, and ICP-MS attached through an ultrasonic cross flow nebulizer and membrane desolvator are used [52].

The separation of PGM in "ng- and subng-" levels from the matrix components is obligatory after the sample decomposition prior to the application of all the above methods because of serious interferences of matrix components in real samples. For the precedent separation and preconcentration, the electrodeposition on carbonaceous material [16], anion exchangers and especially the SPE by hydrophobic bare, derived or modified sorbents, fibres and sorbent powder—fibres mixtures are used and the retained PGM species are then eluted for final determination.

Decomposition of Samples

Dust filters with airborn particulates of metrologic stations could be successfully leached with HNO_3 and H_2O_2, samples of engine soot were decomposed in low-pressure oxygen high-frequency plasma [45] prior to analysis by ICP-AES or ICP-MS. Mixtures of HCl, HNO_3, and HF are suitable for the decomposition of road dust or soil using microwave oven with pressurized or open air vessels [10, 20] but high-pressure PTFE bombs [51] or high-pressure ashers [12, 53] can also be used with success. Biotic samples or body fluids are decomposed in microwave oven with mixtures of acids and H_2O_2 or directly analyzed after dilution with ET-AAS or ICP-MS [54]. Excess of acids such as HCl [41] and HNO_3 [45] interferes and must be removed by evaporation in the presence of repeated portions of HCl or HNO_3, respectively.

Preconcentration of PGM by Solid Phase Extraction (SPE)

A variety of sorbents are suitable for the preconcentration and separation of PGM from the inorganic or organic matrix after mineralization. Several common elements do not interfere under validated conditions. Complexes, chelates or ion associates are retained on filled columns of various lengths or short prefabricated cartridges in home-made or commercial arrangement. The elution of the particular PGM species follows with a limited volume of eluent and the elements are determined *via* instrumental methods, especially by GF-AAS, ICP-AES or ICP-MS in off-line or on-line mode. The recovery of element nearly 100 % for a large concentration level, a high enrichment factor with respect to the volume of the primary solution and the increased selectivity for PGM are demanded. The sample solution is sucked under validated conditions *in vacuo* or pushed by a peristaltic pump through the column.

After sample decomposition, the PGM come usually in the form of inert halogenide complexes and the formation of chelates with particular organic reagent, except those of Pd(II) is slow enough or kinetically hindered at room temperature in contrast to the formation of ion associates with cationic species. The formation of retaining PGM species is usually demanded in solutions prior to the interaction with the sorbent. Complexing agents forming water-soluble complexes are more suitable because of not causing clogging of the sorbent column. PGM chelates are often more rapidly formed at elevated temperature in sulfuric or perchloric acid medium containing acetic acid as catalyst or in the presence of nonaqueous solvents. Batch procedures are sometimes preferred for reaching formation equilibrium of kinetically inert PGM chelates but the use of sorbent columns is more advantageous for the practice.

An early review on preconcentration of noble metals and Ag by coprecipitation on inorganic and organic collectors and some complexing sorbents on the basis of polymers, fibres, and cellulose-containing guanidine, rhodanine, alkylpyrazole or 8-sulfanylquinoline groups is only available [56].

Hydrophobic Sorbents with Surface-Immobilized Reagents. PGM Complexes, Chelates or Ion Associates Are Retained

Bare derivatized silica or coated with more or less strongly retained reagent is often used. Octadecyl silica gel in 3 cm cartridges (particle size 7 μm), was suitable for the almost quantitative preconcentration of 2—20 μg of platinum(IV) as hexachloroplatinate from 0.1 M-HCl in the presence of cationic surfactant dimethyllaurylbenzylammonium bromide. 96 % ethanol was a suitable eluent of the $PtCl_6^{2-}$ ion associate. Cetylpyridinium bromide behaves similarly but the elution of the Pt(IV) ion associate from the column demands higher volumes of ethanol which may interfere with the subsequent ICP-AES. The recovery for platinum was 86—110 % [42] and the sample volume and concentrations of PGM do not influence the recovery of PGM in a limited interval.

Satisfying results for preconcentration of PGM were obtained when ion associates of their chloro complexes with the *N*-[1-(ethoxycarbonyl)pentadecyl]-trimethylammonium bromide (Septonex®) were used. Samples containing 0.1 M-HCl, 0.006 M surfactant and 1—20 μg of PGM were pumped (1 cm^3 min^{-1}) through the octadecyl silica gel column (1 cm^3 of sorbent, particle size 60 μm). The eluate with 96 % ethanol was evaporated in the presence of 0.1 M-HCl and the aqueous solution of the residue was analyzed with ICP-AES and ICP-MS. The recoveries were (100 ± 3) % and (100 ± 1) % for 1—20 μg Pt and Pd from 50 cm^3 of pure solutions. Os and Ir were retained by 90 %. Very poor recoveries were observed for Ru(IV) and Rh(III). The retention decreases with increasing sample volume and in the presence of common metal ions excess, NO_3^- interferes [45]. At present, the sorption of ion associates of PGM chloride, bromide or thiocyanate complexes with a variety of cationic surfactants on various derivatized silica gels is being studied and validated [57].

Aminopropyl and sulfanyl substituted ligands were also immobilized on silica gel. The dynamic capacities of each gel were evaluated for Pd(II) or Rh(III). The retention of Ag(I), Au(III), Ir(III), Os(IV), Pd(II), Pt(IV), Rh(III), and Ru(III) was evaluated in a batch procedure by ICP-AES. Finally metal ions were retained on columns and eluted at different pH [58].

Silica gel derivatized by phenyl- and benzoylthiourea was also successfully used. Distribution coefficients for noble metals 10^2—10^5 cm^3 g^{-1} have been mentioned. Pt(II), Pd(II), and Au(III) were eluted by thiourea solutions in the form of their stable chelates and could be determined by atomic spectrometry [59].

Silica gels C18 and C8 covered with *N*,*N*′-dialkyl-*N*′-benzylthiourea retain Pd(II) quantitatively in the form of a complex from 1—2 M-HCl. The column was rinsed with diluted HNO_3 and Pd(II) finally eluted from the column with ethanol into the GF of AA-spectrometer [60].

The retention of Ir(IV), Rh(III), Pt(IV), Ru(IV), Os(VIII), Pd(II), and Au(III) from aqueous solutions by silica gel modified with nitrogen-containing organic ligands from diluted hydrochloric acid has also been recommended. The interaction of noble metal complexes with the sorbent-containing monoamine groups seems to run *via* complexation at pH > 1, but at pH < 1 according to anion-exchange mechanism. Especially silica gels containing aliphatic mono- and polyamines have a high sorption rate for noble metals. The desorption of the noble metal ions was, however, a complicated process and the authors preferred the final determination by X-ray fluorescence and emission spectrometry of the sorbent phase [61]. The retention of Pt(II), Pd(II), Au(III), Ag(I), Cd(II), and Hg(II) on silica gel containing *N*-propyl-*N*′-

[1-(2-sulfanylbenzthiazolyl)-2,2,2-trichloroethyl]urea (TBTS) was also suitable [62].

Silica gel modified by aminopropylbenzoylazo-1-(2-pyridylazo)-2-naphthol was used for the separation and preconcentration of 20 μg of Pd(II) or Pt(IV) in the form of chelates from 0.1 M-HCl and in the presence of 200 μg of La(III), Cu(II), and Ni(II), 170 μg of Hf(IV), and 500 μg of Cr(III) and Zr(IV). Pd(II) and Pt(II) were successively eluted with a solution of 0.03 M thiourea in 0.1 M-HCl and determined by spectrophotometry. The recoveries for Pd and Pt were 98 % and 96 % and the enrichment factor was 143. The modified sorbent is stable from 6 M-HCl to pH 6 and can be repeatedly used [63]. Silica gels containing adsorbed dithizone, 4,4-bis(dimethylamino)thiobenzophenone or 4-(2-thiazolylazo)naphthol from their solutions in hexane are also suitable to retain Pt(II) and Au(I) [64] but no details are available.

Bis(carboxymethyl)dithiocarbamidate (CMDTC), bis (2-hydroxyethyl)dithiocarbamidate (HEDTC) but also *N*-methylfurohydroxamate (*N*-MFHA) and *N*-(dithiocarboxy)sarcosine (DTCS) give chelates with heavy metal ions and some PGM which may be readily retained on XAD-Amberlite® sorbents. Pt(II), Rh(III), Pd(II) are successfully retained as CMDTC chelates from 1—3 M-HCl solutions in the presence of $SnCl_2$ and reagent excess on microcolumns of XAD-4 macroporous resin (particle size 50—100 μm), later eluted with 5 M-NH_3 or 0.5 M-NH_3 and on-line determined with GF-AAS or ICP-AES using a segmentation technique for the continuous flow. The previous formation of PGM chelates in solutions is completed after 60 min. The retention of PGM chelates is partly hindered by the presence of heavy metal ions, such as Fe(III) or Cu(II). Os and Ir have not been retained under such conditions. With the AAS detection, detection limits 0.03 ng, 0.1 ng, and 0.01 ng for Pd(II), Pt(II), and Rh(III) were given [33], respectively. The Pt(II) chelates with CMDTC obtained from Pt(IV) by the reduction with $SnCl_2$ are adsorbed on Amberlite XAD-4 resin and may also be back-eluted with ethanol. The ethanol was evaporated and the residue was dissolved in 0.14 M-HNO_3. In this way Pt is separated from most matrix elements. Recoveries for Pt were 62—102 % and the detection limit was 1 pg [47]. The commonly used pyrrolidinecarbodithioate on C18 bonded silica gel may also be used for the preconcentration of PGM [65].

Pd(II) and Au(III) are rapidly retained from a medium containing 0.4 M-NaBr, 0.01 M-KSCN, and 0.05 M-HNO_3 on the macroporous sorbent XAD-7 (0.18—0.25 mm) at flow rates 8—10 cm^3 min^{-1} The retained metals were eluted with acetone, the eluate evaporated and the residue dissolved by 0.4 M-NaBr in 0.05 M-HNO_3. The absorbance was measured at λ = 377.4 nm and 332.7 nm for the determination of Au and Pd, respectively [66]. Moreover, the retention also follows in the presence of 3 M-HCl, 25 % KSCN, and 20 % $SnCl_2$. After elution of PGM with acetone, evaporation of the organic solvent and dilution with 25 % KSCN, 20 % $SnCl_2$, and 3 M-HCl the absorbance was measured at 400 nm [67].

Silica gel (S-120, fraction 0.2—0.35 mm) was modified by some organic azo dyes, namely PAN, PAR, TAN, TAR for the retention of Pd(II) besides of Co(II) in the form of chelates and the metals were determined by spectrophotometry after elution [68]. The reaction of heterocyclic hydroxy-substituted azo dyes (HCA) with most PGM is kinetically hindered and chelates are often formed at elevated temperature only. The chelate formation, however, does not take place in the HCl medium from inert PGM halogenide complexes. The reaction is improved from PGM sulfates or perchlorates or in the presence of dioxane or dimethylformamide. The conversion of PGM halogenide complexes to sulfate succeeds during heating the solution with sulfuric acid and acetate. Pd(II) chelates with HCA are formed most easily in perchlorate medium but excess of chloride also interferes strongly.

By using ethylenediamine modified poly(vinyl chloride) (particle size 0.32—1.25 mm) Pd(IV), Pt(IV), Ir(IV) have been surprisingly retained from waste waters. Pd(II) and Au(III) were eluted with 10 M-HCl containing 2 % thiourea, Pt(IV) with a mixture of 10 M-HCl and concentrated HBr and Ir(IV) with a mixture of $NaNO_2$, NH_4I, and KI solutions. The recoveries were 93.3—100 % and metals were finally determined by ICP-AES [69].

Polyurethane foam is a suitable sorbent for inorganic species from solutions containing metal halogenide and thiocyanate complexes in sulfuric, nitric, and hydrochloric acid media [70]. The retention is influenced by the properties of the retained complex species as well as by the solution composition [71]. Pt(IV), Pd(II), Au(III) and other metal ions were successfully retained on polyurethane foam coated by immobilized 4-adamantyl-2-(2-hydroxy-1-naphthyl)thiazole (AOT) [62]. Complicated ternary species of PGM in the presence of 50 % KI, 0.5 M-$SnCl_2$ in 2.4 M-HCl and 1.2 M-HCl are also retained on cubes of polyurethane foam. After preconcentration the metal contents were determined by flame AAS or ICP-AES. Recoveries/% were 99.2; 98.6; 97.8; 98 or 97.8 for Pt, Pd, Rh, Ir, Au, respectively [72].

Complexing or Chelating Sorbents

Sorbents have also been synthesized and the chelating functional analytical group covalently incorporated in the sorbent skeleton of various origin.

A macroporous chelating resin containing thiosemicarbazide (TSC) is suitable for the preconcentration of Pt(IV), Pd(II), and Au(III) from 1.5 M-HCl. The elution of the elements was followed by 5 % thiourea solution with a 97—107 % recovery and metals were determined by AAS [73].

Noble metal ions, especially Pd(II) and Pt(IV) may also be retained at pH 1—7 on a chelating resin prepared by the reaction of dithizone with a chloromethylated poly(vinyl pyridine) resin. Pd and Pt were desorbed from the resin with 1 % or 5 % thiourea in 0.1 M-HCl [74].

The chelating macroporous resin containing imidazolinylethylamino functional groups retains chloride complexes of Pt(IV) and Pd(II) from diluted HCl. The retained species were quantitatively desorbed with 4 % thiourea in 0.25 M-H_2SO_4 with a 90—110 % recovery and finally determined by ICP-MS [75].

A macroporous resin with poly(vinylaminoacetone) chelating groups (PVAA) can be synthesized readily. This resin is suitable for preconcentration and separation of traces of Au(III), Pd(IV), Rh(III), and Ru(III) under solutions flow rate 1.5 cm^3 min^{-1} After elution from the column by mixed 6 M hydrochloric acid and 3 % thiourea solution, traces of Au, Pd, Rh, and Ru were determined by ICP-AES. Interferences by common metals were not observed in real samples. Recoveries of these elements in nonferrous matrices were above 95 % with the RSD between 2.0 % and 4.0 % [76].

A spherical macroporous epoxy-imidazole complexing resin has been found suitable for preconcentration and separation of traces of Pd(IV), Ru(III), and Au(III) from diluted HNO_3 and HCl solutions in dependence on pH as well as the subsequent elution by 5—6 M-HCl containing thiourea. The metals were finally determined by ICP-AES. A 100-fold excess of common metal ions causes little interferences [77].

Similarly a macroporous poly(vinylthiopropionamide) resin retained Pt(IV), Pd(II), and Ir(III) from solutions at different pH. The elution of PGM followed by 6 % thiourea in 1 M-HCl and 6 M-HCl for Ir(III) respectively and the metals were determined by ICP-AES. Traces of Pt(IV) and Pd(II) were enriched quantitatively in the range of 5 M-HCl to pH 9. Recoveries were higher than 96 %, for traces of Ir > 93 % between pH 1—9. The retention of Ru(III) or Rh(III) at pH 3—6 was incomplete [78].

A chelating resin containing 2-aminopyridine functional groups was recommended for the retention of Rh(III), Ir(III), Pt(II), and Pd(II). Common metal ions were eluted by 0.5 M-HCl and finally the PGM with a mixture of 4 M-HCl and 2 M-$HClO_4$. Their final determination has been carried out with ICP-AES [79]. An on-line flow system with a microcolumn of ion exchanger resin containing 2-aminopyridine has been described for the retention of Pd(II), Pt(IV), and Ir(III) [80]. The column was successfully rinsed with 6 M-HCl, H_2O, 6 M-NaOH, and water and the PGM eluted by a mixture of 0.5 M-HCl, 0.5 M-$HClO_4$, and 0.5 M-$MgCl_2$ and determined with FAAS in acetylene—air flames [80].

A resin containing polydithiocarbamate retains Pt(II) and Pd(II) besides of Au(III) and Ag(I). The solution was passed through a small column of poly(dithiocarbamate) resin (0.16—0.25 mm). The resin was then dried at 80 °C and decomposed with 50 % H_2O_2 at 230 °C for 4 h. After evaporation, the resin residue was dissolved in 2 cm^3 of 1 M-HNO_3 and the noble metals were determined by ICP-AES. The recoveries were 93—99 % [81].

2-Methyl-1,3,5-oxathiazepine-4-thione, a homopolymer of 2-(vinyloxy)ethylisothiocyanate, and a homopolymer of *N*,*N*′-bis(vinyloxyethyl)thiuramdisulfide were synthesized and studied with respect to the sorption ability towards Pt-metals, Au, Ag, and Hg. All compounds retain metal ions in 1—6 M acid solutions. Under these conditions, the separation of PGM, Au, Ag, and Hg is possible from large amounts of Fe, Cu, Ni, Co, Zn. The retention of PGM depends on concentration and nature of acid and the nature of complexes in solution [82].

A chelating resin YPA-4 (no information about its structure) is described to retain PGM from 2.5 M-HCl. After careful rinsing, the resin was ashed after addition of graphite. The residue was vaporized by laser ablation into ICP atomic emission spectrometer. Detection limits were 0.7 ng g^{-1} for Pd, Pt, Rh, and Ru and 0.6 ng g^{-1} for Ir and Os [83].

Russian chelating sorbents POLYORGS on the basis of styrene copolymers, glycidyl derivatives, alkylated cellulose, aminopolystyrene, and fibrous acrylonitrile containing pyrazole, imidazole, amidoxime, 2-sulfanylbenzothiazole, thioglycolanilide or bisazo dyes with characteristic function-analytical groups as components show increased selectivity for heavy metal ions, lanthanoids, and noble metals. They are suitable for the preconcentration of metals during the analysis of ores, rocks, waters, and industrial products. After preconcentration in batch or column procedures the metal species are eluted or the sorbent decomposed by acid ashing with graphite or applied in suspension in DMF and the metal traces determined by GF-AAS, AES, ICP-AES or X-rays emission spectrometry. Especially POLYORGS with 3,5-dimethyl- or 5-methylpyrazolone, pyrazolazo and benzimidazole components are suitable for the preconcentration of PGM and Au, Ag from 50—300 cm^3 of 0.1—2 M hydrochloric acid at room temperature or in microwave oven at 100 °C, using 0.1—0.2 g of the sorbent [34, 84].

The metals were also concentrated on POLYORGS sorbent based on the copolymer glycidylmethacrylate—ethylene—dimethacrylate [85, 86] by shaking with 1 M hydrochloric acid containing 0.01—1 $\mu g\ cm^{-3}$ of the metals for 1 h. The sorbent was filtered off and decomposed by 10—15 min heating with 1 M-HCl at 80 °C and the solution analyzed by ET-AAS. Pd, Pt, and Rh were determined spectrophotometrically at λ = 244.8 nm, 265.9 nm, and 343.5 nm, respectively.

The limits of detection were 80 pg of Pt, 26 pg of Pd, and 18 pg of Rh [85].

A chelating resin containing *N*,*N*′-dialkylbenzoylthiourea has increased affinity towards Pd(II), Pt(IV), Ru(III), Ir(III) but lowered affinity against heavy common metal ions which is advantageous for the separation of PGM. The elution is carried out by 0.2 M thiourea in 0.1 M-HCl with a high recovery [87].

Similarly chelating resins containing SH groups are suitable for the preconcentration of Pd(II), Pt(IV), and Au(III) from aquatic medium. Contamined ions were rapidly eluted with 0.1—0.2 M-KCN but the elution of adsorbed Os(VIII) and Ir(IV) was difficult [88].

In addition, PGM metals are recovered by sorbents with aliphatic or heterocyclic amino groups from hydrochloric acid solutions ($c_{\mathrm{HCl}} > 1$ mol dm^{-3}) due to the interaction with protonated positively charged sorbent amino groups. The most effective recovery of platinum metals was obtained on the sorbent based on weakly cross-linked polystyrene containing diethylenetriamine groups [89—91]. Under these conditions, the 95—99 % recoveries of Ru(IV), Rh(III), Pd(II), Ir(III, IV), Pt(IV) were obtained even in the presence of 10^6—10^7 amounts of Cr(III), Fe(III), Ni(II), Cu(II) and sulfate. The PGM were finally determined by ET-AAS. Platinum metals were also retained from chloride solutions by solid extraction of hydrophobic ion associates of anionic chloride complexes with protonated *N*′-(dodecyl)diethylenetriamine containing sorbent [43, 92].

Silica gels modified with amine, ammonium, guanidinium, morpholinium or triphenylphosphonium groups are also suitable for the preconcentration of chloride complexes of PGM and Au. Equilibrium was reached after shaking for 10 min. After separation of the sorbent, the noble metals were determined by ICP-AES or by luminescence with 1,10-phenanthroline in the case of Os. All five derived sorbents exhibited high distribution ratios for all metals [93].

Fibrous Complexing Sorbents

Chelating sorbents may be used in the form of granules, powders, and fibres. Fibrous complexing sorbents possess essential advantages for preconcentration with respect to increased speed of sorption and suitability of preconcentration procedure. Fibrous complexing sorbents were synthesized with different functional groups on the base of polyacrylonitrile, poly(vinyl alcohol) or cellulose. Sorbents containing amine, heterocyclic amine, and 2-mercaptobenzothiazole groups are suitable for the preconcentration of noble metals.

A special kind of fibrous sorbents are those filled with a complexing ion exchangers. Thus, filled materials consist of two polymers, in the fibrous and powdered forms. The powdered polymer is well retained in the fibre and has a good contact with solution. PGM retained by fibrous complexing sorbents are finally determined by means of AAS, ICP-AES, XRF [95].

By using polyacrylacylisothiourea chelating fibres, Au(III), Pd(IV), and Ru(III) are satisfactorily enriched and separated from samples with satisfactory results and determined by ICP-AES [96].

A poly(acrylamidrazone-hydrazide) chelating fibre packed in a glass column has also been used to retain PGM from sample solutions adjusted to pH 2—4. The elution of PGM was effected with a mixture of 6 % H_2SO_4, 2.5 % thiourea and Au and Pd were determined by ICP-AES. The fibres gave recoveries of > 95 % and were regenerated by washing with 12 M-HCl or 15 M-HNO_3 followed by dilute NH_3 solution and water [97].

Fibres of the copolymer of acrylonitrile with 2-methyl-5-vinylpyridine were also chosen for preconcentration and separation of platinum metals and gold. Pyridine groups in the sorbent phase cause anion-exchange properties of the fibre [98].

Columns with activated carbon fibre (ACF) were used for the quantitative preconcentration of Pd(II) from solutions with pH 3.0. The elution followed by 1—1.5 % thiourea in 1 M-HCl with a recovery 103—107 % for Pd. The final determination was carried out by ET-AAS or ICP-MS [99].

Grain and fibre carbon materials were found to be selective to micropreconcentration of Pd(II), Rh(III), Ru(IV), and Ir(III) after separation from 100—1000-fold excess of common metals (Cu, Zn, Al, Cr, Mn, Fe, Co, Ni) in technological samples. The final determinations of PGM were carried out after elution by selective kinetic or spectral procedures [100].

PGM, especially Pt(IV) or Pd(II), may also be effectively retained on activated carbon from water acidified with 12 M-HCl during a batch procedure. After filtration, the carbon containing the PGM was ashed at 650 ℃, the ash dissolved in aqua regia and the solution analyzed by ICP-MS. Detection limits for Pd and Pt were 0.8 ng dm^{-3} and 0.4 ng dm^{-3} and the enrichment factor was 200 for 1 dm^3 sample volume [48].

Sorbents Coated with Liquid Anion Exchanger and Extracting Agents

Extraction on columns with hydrophobic or inert sorbents is suitable for the separation or preconcentration of elements with similar properties, *i.e.* similar distribution coefficients or stability constants of their complexes. The repeated extraction act on the column is advantageous for the retaining of metal traces in the presence of excess of macrocomponent. The inert sorbent is previously coated by the ion-pairing or chelating agent in low-polar solvent whereas the mobile phase is the aqueous metal solution. This procedure is rather limited for PGM because of the slow formation of PGM chelates.

Rh(III), Ru(IV), Pd(II), Pt(IV), Ir(III), Os(IV), and Au(III) may be extracted with trioctylamine coated on hydrophobic teflon. The particular metal species were then reextracted from the sorbent by mixtures of 1—6 M-HNO_3 and HCl or by 5 % thiourea—1 M-HCl mixture. The recoveries for PGM were 92.5—99 % and the final determination was carried out by AAS or ICP-MS [104]. For preconcentration of Pd, tribenzylamine was also used [105].

Silica gel C18 covered by methyltricaprylammonium chloride (Aliquat 336) retains platinum. The platinum species were eluted from the column by a mixture of 1 M-HCl—0.1 M-$HClO_4$ and directly sampled into the nebulizer of the ICP-MS. Such procedure was used for the determination of Pt in tunnel dust after its decomposition by aqua regia and H_2O_2 in a microwave oven. The detection limit was 0.17 ng Pt [106].

Synthetic samples containing 21 basic metals and 5 noble metals were dissolved and the solutions diluted with 1 M-HCl. A portion of the solution was shaken for 1 h at 25 °C with 0.2 g of trioctylamine containing resin as a group reagent. The solid substance was filtered off and boiled gently to dissolve in 8 cm^3 of $HClO_4$—HNO_3 ($\varphi_r = 1 \quad 1$). PGM were determined by ICP-AES. The recovery of PGM has been 90—102 % [94].

Pd(II) is retained on PTFE columns by PAN solution in $CHCl_3$ at pH 2—3 or isopentanol solution at pH 2.5—3.5 or their mixture ($\varphi_r = 1 \quad 1$) from the sulfate and acetate containing mobile phase. The enrichment factor is about 100 [101, 102]. For other PGM such as Pt(II) or Rh(III), a heating of the column to 85 °C and a low flow rate of the aqueous solution of PGM are necessary for the successful retention. At room temperature the separation of Pd from other PGM is only possible. Several common metal ions have been screened by EDTA [103].

Pd(II), Pt(II), and Rh(III) were also retained from their sulfate solutions (pH 3.0 to 3.8) containing Na acetate and 1 M-H_2SO_4 at 85 °C by a column of PTFE carrying 4-(2-pyridilazo) resorcinol (PAR) in isopentanol and the chelates were reextracted from the cooled column with $CHCl_3$—isopentanol ($\varphi_r = 2 \quad 1$). The three components in the eluate can be determined spectrophotochemically in the form of their PAR chelates or separated by HPLC on a column of polar silica gel (Silasorb 600®) with benzene—propan-2-ol ($\varphi_r = 9 \quad 1$) as mobile phase and detected at 440 nm. The enrichment factor was nearly 100 in this way [107].

Pt(II), Pd(II), Rh(III), Ir(III) chelates are also extracted with 1-(2-pyridylazo)-2-naphthol (PAN) in isoamyl alcohol coated on Teflon® (particle size 0.1—0.2 mm) from sulfate medium at pH 3.0—3.8 [108, 109].

Solid-supported liquid membranes containing liquid anion exchanger as a carrier are now more frequently used for selective transport of PGM from sample solutions.

A PTFE membrane impregnated with trioctylamine in kerosene was modified with octan-1-ol for extraction of Pt(IV), Pd(IV), and Au(III) species from the outer solution containing HCl. The noble metals were stripped into 1 M-$HClO_4$ placed in the inner compartment of a polypropylene device. The transport across the membrane for Pt(IV) and Pd(IV) was enhanced by higher trioctylamine concentrations [110]. A liquid kerosene membrane containing tridecanol and 7-dodecenyl-8-quinolinol enhanced the transport of Pt(IV) from diluted HCl or H_2SO_4. On the other hand, Pd(II) was retained in the membrane if transported from H_2SO_4 or HNO_3 solutions [124]. The separation and enrichment of traces of Pd(II) (as $PdCl_4^{2-}$) from aqueous solution was performed by means of emulsion membrane. The composition of the organic phase in the membrane was 5 % trioctylamine, 10 % monobutanediimide, 10 % liquid paraffin oil as membrane modifier, and 75 % kerosene as membrane solvent. The 5-fold excess of aqueous phase consisted of 11 % NH_3, and the optimal volume proportion of organic and aqueous phase was 2 1. Pd was finally determined by flame AAS. Best recoveries for Pd by 96 % with RSD of 1.1 % were from a sample solution containing 1 $\mu g\ cm^{-3}$ Pd, 1 mM-NaCl and 0.1 M-HCl. Large excess of common metal ions only interferes [111]. Similarly $IrCl_6^{2-}$ could be transported through a supported liquid membrane from diluted HCl into small volume of 1 M-$HClO_4$ [125]. A microporous polydifluoroethylene film was impregnated with Aliquat 336 and used to separate mixtures of Rh, Pd, and Pt. A feed solution containing 10 mg dm^{-3} of each Rh, Pd, and Pt and 1 mM-SCN^- was extracted and Pt and Pd were transported into the stripping solution while Rh remained in the feed solution because $Rh(SCN)_6^{3-}$ had not been formed [112].

Common Basic Anion Exchangers

Common strongly basic anion exchangers Dowex 1 based on the styrene—divinylbenzene copolymer strongly retain PGM from solutions containing chloride and thiocyanate complexes in the presence of diluted HCl. The separation and preconcentration of PGM in the form of inert chloride complexes on basic anion exchanger has been frequently used [44, 113—119]. The retention has been performed from hydrochloric acid solutions or mixtures of diluted HCl, HNO_3, and HF. Common matrix metal ions can be previously eluted, for the strongly retained PGM anions 11 M-HCl or 13.5 M-HNO_3 for Ru, Pd, Pt, Ir [118], hot 6 M-HCl for Rh and diluted NH_3 for Pd and Pt(IV) [117], 0.3 M thiourea with 0.1 M-HCl for Ru, Pd, Pt, and part of Rh and 12 M-HCl for Ir(IV) and the rest of Rh [116], and 0.5 M-$NaClO_4$ for Pt(IV) [119] have also been used. The strongly acid cation exchanger Amberlite CG-120® is more suitable for the retention of PGM from 0.2 M-HCl. The recovery > 95 % results for Pd(II), Ru(IV), Rh(III), Ir(III), Pt(IV), and Au(III) after elution with 2.5 M-HCl [113].

Amberlite IRA 416® and Amberlite IRA 910® type anion exchangers were also suitable for the retention of chloro complexes of gold(III) and palladium(II) in hydrochloric acid media. A good separation of Au and Pd chloro complexes can be achieved in spite of the small selectivity of this kind of resins [121]. Increased amounts of eluting agents and salts interfere with the subsequent spectrochemical methods and must be previously removed.

For analysis of dust, ion-exchange separation was used after digesting samples in pressurized vessels of microwave oven. The residue after evaporation was dissolved and submitted to the ion exchanger column in 0.5—0.3 M-HCl. Pt(IV) retained on the column was eluted with nitric acid at 90 ℃ and analyzed by isotope dilution ICP-MS. The recovery for 10 ng of Pt was > 60 % and the detection limit 1.4 ng g^{-1} [120].

A column packed with a Chinese HHY-10A macropore anionic resin has been used for the retention and desorption of ^{199}Au and ^{195m}Pt from 0.5 M-HCl. The column was washed with 0.1 M-HCl and the radioisotopes eluted with 2 % thiourea. Under optimal conditions, the recoveries were (92.3 ± 2.6) % for Au and (97.7 ± 0.9) % for Pt [122].

Aluminium oxide activated with 0.1 M-HNO_3 also retains $PtCl_6^{2-}$ from pH 2.5 and HCl medium with surprisingly 100 % efficiency under optimized conditions. The elution took place with 2 M-NH_3. Excess of inert salts and chlorides considerably interferes [123].

CONCLUSION

Most convenient methods for the determination of platinum and other PGM metals in environmental and biotic material are usually ET-AAS, ICP-AES, and ICP-MS which show sufficient sensitivity and detection power but precedent separation and preconcentration of PGM must be carried out. For this purpose solid phase extraction (SPE) may be used with advantage. The retention of ion associates of PGM halogenide complexes with cationic surfactants such as *N*-[1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Septonex®) on columns with bonded C18 or C8 silica gel and coated with the surfactant is highly efficient from hydrochloric acid medium. The formation of ion associates is fast enough and the retention as well as the elution with ethanol proceeds rapidly and is quantitative for Pt(IV), Pd(II), Au(III). A drawback is the interference of HNO_3 in solution which must be removed by repeated evaporation with HCl prior to the application of surfactant and interaction with the column. Strongly basic anion exchangers firmly retain PGM as halogenide complexes from HCl medium but there is no selectivity for PGM. Moreover, the elution of PGM from the column is difficult and hot diluted HNO_3, high concentrations of mineral acids, complexing agents or 0.5 M-$NaClO_4$ must be used. The excess of inert salts or complexing agent in the eluate usually interfere with the final ICP-AES or ICP-MS.

The interaction of halogenide complexes of PGM with complexing sorbents or those being modified by coated chelating reagents is kinetically hindered at room temperature with the exception of Pd(II). Thus, the retention of PGM on sorbent columns during the dynamic mode is often insufficient. In such a case the previous formation of PGM chelates in solution is recommended or the previous conversion of PGM halogenides into sulfates in the presence of acetic acid as coordination catalyst at elevated temperature. The highest affinity towards PGM in low valency numbers, especially Pd(II) and Pt(II) is shown by the complexing reagents containing sulfur or nitrogen in the function - analytical group, *e.g.* dithiocarbamidate or thiourea derivatives.

REFERENCES

1. Yi Biu Qu, *Analyst 121*, 139 (1996).
2. Balcerzak, M., *Analyst 122*, 67R (1997).
3. Pyrzynska, K., *Talanta 47*, 841 (1998).
4. *Platinum, Environmental Health Criteria 125.* World Health Organization, Geneva, 1991.
5. Klueppel, D., Jakubowski, N., Messerschmidt, J. Stuewer, D., and Klockow, D., *European Winter Conference on Plasma Spectrochemistry*, 12—17 January, 1997, University of Gent, Gent, Belgium, 1997.
6. Redijk, J., *Pure Appl. Chem. 59*, 181 (1987).
7. Abrams, M. J. and Murrer, B. A., *Science 261*, 726 (1993).
8. Hodge, V F. and Stallard, M. O., *Environ. Sci. Technol. 20*, 1058 (1986).
9. Eller, R., Alt, F., Tölg, G., and Tobschall, H. J., *Fresenius' J. Anal. Chem. 334*, 723 (1989).
10. Colodner, D. C., Boyle, E. A., and Edmond, J. M., *Anal. Chem. 65*, 1419 (1993).
11. Georgieva, M. and Pihlar, B., *Anal. Lab. 4*, 224 (1995).
12. Alt, F., Bambauer, A., Hoppstock, K., Mergler, B., and Tölg, G., *Fresenius' J. Anal. Chem. 346*, 693 (1993).
13. Wildhagen, D. and Krivan, V., *Anal. Chim. Acta 274*, 257 (1993).
14. Schlögl, R., Indlekofer, G., and Oelhafen, P *Angew. Chem. 99*, 312 (1987).
15. Farago, M. L., Kavanagh, P. Blank, R., Kelly, J. Kazantzis, G., Thorton, I., Simpson, P R., Cook, J. M., Parny, S., and Hall, G. M., *Fresenius' J. Anal. Chem. 354*, 660 (1996).
16. Beinrohr, E., Lee, M. L., Tschöpel, P., and Tölg, G., *Fresenius' J. Anal. Chem. 346*, 689 (1993).
17. Schramel, P. Wendler, I., and Lustig, S., *Fresenius' J. Anal. Chem. 353*, 115 (1995).
18. Messerschmidt, J., Alt, F., and Tölg, G., *Anal. Chim. Acta 291*, 161 (1994).

19. Hall, G. E., Pelchat, J. C., and Dunn, C. E., *J. Geochem. Explor. 37*, 1 (1990).
20. Begerow, J., Turfeld, M., and Dunemann, L., *Anal. Chim. Acta 340*, 277 (1997).
21. Kolpakova, N. A., Antipov, S. A., and Kaminskaya, O. V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract G-27.
22. Begerow, J. and Dunemann, L., *J. Anal. At. Spectrom. 11*, 303 (1996).
23. Einhäuser, T. J. Galanski, M., and Keppler, B. K., *J. Anal. At. Spectrom. 11*, 747 (1996).
24. Balcerzak, M. and Donard, O. F. X., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract N-18.
25. Matusiewicz, H. and Barnes, R. M., *Acta Chim. Hung. 125*, 777 (1988).
26. Nyrgen, O., Vaughan, G. T., Florence, T. M., Morrison, G. M. P., Warner, I. M., and Dale, L. S., *Anal. Chem. 62*, 1637 (1990).
27. Casetta, B., Roncadin, M., Montanari, G., and Furlanut, M., *At. Spectrosc. 12*, 81 (1991).
28. Van Warmerdam, L. J. C., Van Tellingen, O., Maes, R. A. A., and Beijnen, J. H., *Fresenius' J. Anal. Chem. 351*, 777 (1995).
29. Wei, Ch. and Morrison, G. M., *Anal. Chim. Acta 284*, 587 (1994).
30. Alt, F., Eschnauer, H. R., Mergler, B., Messerschmidt, J., and Tölg, G., *Fresenius' J. Anal. Chem. 357*, 1013 (1997).
31. Korda, T. Buchbinder, G., Kalish, N. and Torgov, V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract O-20.
32. Torgov, T., Demidova, M., Korda, T., Kalish, N., and Shulman, R., *Analyst 121*, 489 (1996).
33. Lee, M. L., Tölg, G., Beinrohr, E., and Tschöpel, P. *Anal. Chim. Acta 272*, 193 (1993).
34. Kuz'min, N. M., Kubrakova, I. V., Pukhovskaya, V. M., and Kudinova, T. F., *J. Anal. Chem. 49*, 182 (1994).
35. Calmotti, S., Dossi, C., Recchia, S., and Zanderighi, G. M., *Spectrosc. Eur. 8*, 18 (1996).
36. Watson, A. E., Russell, G. M., Middleton, H. R., and Davenport, F. F., *Rep. MINTEK M81*, 13 (1983).
37. Graham, S. M. and Robert, R. V. D., *Talanta 41*, 1369 (1994).
38. Hoppstock, K., Alt, F., Cammann, K., and Weber, G., *Fresenius' J. Anal. Chem. 335*, 813 (1989).
39. Ulakhovich, N. A., Budnikov, G. K., and Medyantseva, E. P *Zh. Anal. Khim. 47*, 1546 (1992).
40. Rietz, B. and Heydron, K., *J. Radioanal. Nucl. Chem. 174*, 49 (1993).
41. Paukert, T., *Chem. Listy 87*, 8 (1993).
42. Otruba, V., Strnadová, M., and Skalníková, B., *Talanta 40*, 221 (1993).
43. Kubrakova, I. V. Kudinova, T. F., Kuz'min, N. M., Kovalev, I. A., Tsysin, G. I., and Zolotov, Yu. A., *Anal. Chim. Acta 334*, 167 (1996).
44. Hodge, V., Stallard, M., Koide, M., and Goldberg, E. D., *Anal. Chem. 58*, 616 (1986).
45. Vlašánková, R., Otruba, V., Bendl, J., Fišera, M., and Kanický, V., *Talanta 48*, 839 (1999).
46. Totland, M., Javis, I., and Jarvis, R. E., *Chem. Geol. 104*, 175 (1993).
47. Parent, M., Vanhoe, H., Moeus, L., and Dams, R., *Fresenius' J. Anal. Chem. 354*, 664 (1996).
48. Hall, G. E. and Pelchat, J. C., *J. Anal. At. Spectrom. 8*, 1059 (1993).
49. Dams, R. F. J., Goossens, J. and Moens, L., *Mikrochim. Acta 119*, 277 (1995).
50. Wegscheinder, W. and Zischka, M., *Fresenius' J. Anal. Chem. 346*, 525 (1993).
51. Jerono, U. Alt, F., Messerschmidt, J., and Tölg, G., *Mikrochim. Acta 108*, 221 (1992).
52. Lustig, S., Michalke, B., Beck, W., and Schramel, P *Fresenius' J. Anal. Chem. 360*, 18 (1998).
53. Alt, F., Jerono, U., Messerschmidt, J., and Tölg, G. *Mikrochim. Acta III, 1988*, 299.
54. Di Noto, V., Ni, D., Dalla Via, L., Scomazzon, F., and Vidali, M., *Analyst 120*, 1669 (1995).
55. Mukai, H., Ambe, Y., and Morita, M., *J. Anal. At. Spectrom. 5*, 75 (1990).
56. Myasoedova, G. V. and Malofeeva, G. I., *Zh. Anal. Khim. 34*, 1626 (1979).
57 Vlašánková, R. and Sommer, L., to be published.
58. Schilling, T., Schramel, P., Michalke, B., and Knapp, G., *Mikrochim. Acta 116*, 83 (1994).
59. Losev, V., Bakhvalova, I., Volkova, G., Mazniak, N., and Trofimchuk, A., *International Congress on Analytical Chemistry,* Moscow, Russia, June 15—21, 1997, Abstract C-26.
60. Schuster, M. and Schwarzer, M., *Anal. Chim. Acta 328*, 1 (1996).
61. Tikhomirova, T. I., Fadeeva, V. I., Kudryavtsev, G. V., Nesterenko, P N., Ivanov, V. M., Savitchev, A. T., and Smirnova, N. S., *Talanta 38*, 267 (1991).
62. Dyachenko, N. A., Karetnikova, E. A., Trofimchuk, A. K., and Sukhan, V V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-54.
63. Liu, F., Li, K. A., Wu, Y. S., Wang, X., and Tong, S. Y., *Microchem. J. 52*, 274 (1995).
64. Zaporozhets, O., Petruniok, N., and Sukhan, V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract D-26.
65. Shah, N. K. and Wei, C. M., *J. Radioanal. Nucl. Chem. 130*, 451 (1989).
66. Elci, L., Isildar, S., and Dogan, M., *Anal. Chim. Acta 293*, 319 (1994).
67 Soylak, M., Elci, L., and Dogan, M., *Fresenius' J. Anal. Chem. 351*, 308 (1995).
68. Kuznetsova, O. V. and Ivanov, V. M., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract L-104.
69. Chang, X., Su, Z., Zhan, G., Luo, X., and Xu, Z., *Huaxue Xuebao 48*, 157 (1990).
70. Nabivanets, B., Gorlach, V., and Lysenko, E., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-52.
71. Dmitrienko, S., Pyatkova, L., Myshak, E., Goncharova, L., Gurary, E., and Runov, V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-53.
72. Wu, L. S. and Zhao, M. Z., *Fenxi Huaxue 22*, 877 (1994); *Anal. Abstr. 57*, 3D156 (1995).
73. Yu, Z., Wang, H., Li, C., and Wei, X., *Yangkuang Ceshi 10*, 9 (1991); *Anal. Abstr.* 54, 7E42 (1992).

74. Shah, R. and Devi, S., *Anal. Chim. Acta 341*, 217 (1997).
75. Zu, Z. X., Pu, Q. S., Luo, X. Y., Chang, X. J. Zhan, G. Y., and Ren, F. Z., *Talanta 42*, 1127 (1995).
76. Chang, X., Luo, X., Zhan, G., and Su, Z., *Talanta 39*, 937 (1992).
77. Chang, X. J., Su, Z. X., Yang, D., Gong, B., Pu, Q. S., and Li, S. K., *Anal. Chim. Acta 354*, 143 (1997).
78. Su, Z., Chang, X., Xu, K., Luo, X., and Zhan, G., *Anal. Chim. Acta 268*, 323 (1992).
79. Li, L., Ma, J., and Chen, L., *Gaodeng Xuexiao Huaxue Xuebao 10*, 531 (1989).
80. Di, P and Davey D. E., *Talanta 42*, 685 (1995).
81. Chung, Y. S. and Barnes, R. M., *J. Anal. At. Spectrom. 3*, 1079 (1988).
82. Shaulina, L. P., Golentovskaya, I. P., and Smagunova, M. I., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-68.
83. Duan, Y. R., Li, W. H., and Xu, Y. W., *Fenxi Huaxue 22*, 366 (1994).
84. Myasoedova, G. V., *Fresenius' J. Anal. Chem. 341*, 586 (1991).
85. Stavnivenko, E. B. and Kuz'min, N. M., *Zh. Anal. Khim. 50*, 1243 (1995).
86. Krioukov, S. V., Gabdullin, M. G., Zakharov, S. V. and Garifzianov, A. R., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract L-55.
87. Szczepanik, W., *Chem. Anal.* (Warsaw) *37*, 257 (1992); *Anal. Abstr. 55*, 7D116 (1993).
88. Egawa, H., Jyo, A., and Ochiai, K., *Nippon Kagaku Kaishi 4*, 359 (1994); *Anal. Abstr. 56*, 11D150 (1994).
89. Kovalev, I. A., Tsysin, G. I., Formanovski, A. A., Kubrakova, I. V., Zakharov, V. N., Aslanov, L. A., and Zolotov, Yu. A., *Zh. Anal. Khim. 40*, 828 (1995).
90. Kovalev, I. A., Tsysin, G. I., Formanovski, A. A., Evtikova, G. A., Marov, I. N., Zakharov, V N. Aslanov, L. A., and Zolotov, Yu. A., *Zh. Anal. Khim. 40*, 55 (1995).
91. Kovalev, I. A., Tsysin, G. I., and Zolotov, Yu. A., *Mendeleev Commun. 1995*, 111.
92. Kovalev, I. A., Tsysin, G. I., Kubrakova, I. V., and Zolotov, Yu. A., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-29.
93. Runov, V. K., Strepetova, T. V., Pukhovskaya, V. M., Trofimchuk, A. K., and Kuz'min, N. M., *Zh. Anal. Khim. 48*, 43 (1993).
94. Li, L., Su, X., An, Y., Ma, J., and Yu, S., *Fenxi Shiyanshi 8*, 1 (1989).
95. Shcherbinina, N. I. and Myasoedova, G. V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-5.
96. Chan, G. X., Su, Z. X., Zhan, G. Y., Luo X. Y., and Gao, W. Y., *Analyst 119*, 1445 (1994).
97. Chang, X. J., Zhan, G. Y., Luo, X. Y., and Su, Z. X., *Mikrochim. Acta 112*, 245 (1994).
98. Khmelyov, S. S., Mushtakova, S. P., and Simanova, S. A., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-27.
99. Lin, S. L., Zheng, C. S., and Yun, G. Z., *Talanta 42*, 921 (1995).
100. Tarkovskaya, I. A., Tikhonova, L. P., Rosokha, S. V Korovin, Yu. F., Komarov, V. P., and Kadochnikov, V. A., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-25.
101. Bolshova, T. A., Morozova, N. B., and Ivanov, V M., *Zh. Anal. Khim. 40*, 1394 (1985).
102. Figurovskaya, O. N., Busev, A. I., and Ivanov, V M., *Zavod. Lab. 39*, 132 (1973).
103. Alimarin, I. P Ivanov, V M. Bolshova, T. A., and Basova, E. M. *Fresenius' J. Anal. Chem. 335*, 63 (1989).
104. Li, L., Xu, X., An, Y. and Ma, J., *Fenxi Huaxue 18*, 195 (1990).
105. Tang, F., Mao, X., Wu, G., and Zhang, Y. *Gaodeng Xuexiao Huaxue Xuebao 14*, 271 (1993); *Anal. Abstr. 55*, 10D217 (1993).
106. Akatsuka, K., Hoshi, S., Katoh, T., Willie, S. N., and McLaren, J. W., *Chem. Lett. 9*, 817 (1995); *Anal. Abstr. 58*, 4H23 (1996).
107 Basova, E. M., Ivanov, V. M., Bolshova, T. A., and Babkova, N. A., *Zh. Anal. Khim. 45*, 671 (1990).
108. Timerbaev, A. R., Tsoi, I. G., and Petrukhin, V M., *J. Chromatogr. 448*, 337 (1990).
109. Ivanov, V M., *Geterotsiklicheskie azosoderzhashchie azosoedineniya*, p. 151. Nauka, Moscow, 1982.
110. Fu, J., Nakamura, S., and Akiba, K., *Anal. Sci. 11*, 149 (1995).
111. Wang, Z. X., Li, Y. M., Li, Y. T. and Guo, Y *Anal. Lett. 27*, 957 (1994).
112. Fontas, C., Antico, E., Salvado, V., Valiente, M. and Hidalgo, M., *Anal. Chim. Acta 346*, 199 (1997).
113. Chen, Z., Fryer, B. J. Longerich, H. P., and Jackson, S. E., *J. Anal. At. Spectrom. 11*, 805 (1996).
114. Colodner, P., Boyele, E. A., and Edmond, J. M., *Anal. Chem. 65*, 1419 (1993).
115. Al-Bari, S. J. and Chow, A., *Talanta 31*, 815 (1984).
116. Jarvis, M. M., Totland, M. M., and Jarvis, K. E., *Analyst 122*, 19 (1997).
117. Gaita, R. and Al-Bari, S. J., *Talanta 42*, 249 (1995).
118. Rehkämper, M. and Halliday, A. N. *Talanta 44*, 663 (1997).
119. Krásenský, P and Kanický, V., *Šcr. Fac. Sci. Nat. Univ. Mas. Brun. 27—28*, 75 (1997—1998).
120. Akatsuka, K., Hoshi, S., McLaren, J. W., and Berman, S. S., *Bunseki Kagaku 43*, 61 (1994); *Anal. Abstr. 56*, 8H26 (1994).
121. Sanchez, J. M., Antico, E., Hidalgo, M., Valiente, M., and Salvado V *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-46.
122. Li, C. S., Chai, C. F., Yang, X. F., Hou, X. L., and Mao, X. Y., *Talanta 44*, 1313 (1997).
123. Putnova, P. and Otruba, V., private communication.
124. Fu, J., Nakamura, S., and Akiba, K., *J. Membr. Sci. 107*, 283 (1995).
125. Fu, J., Nakamura, S., and Akiba, K., *Sep. Sci. Technol. 30*, 3821 (1995).

Příloha 2

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A Survey of the Potential of the High Performance Liquid Chromatography and Capillary Zone Electrophoresis for the Determination of Platinum and Platinum Group Metals

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Summary

Various platinum group metals (PGMs) can be separated in the form of complexes with monodentate ligands, ion associates or chelates by high performance liquid chromatography (HPLC) or capillary zone electrophoresis (CZE). Ion associates of anionic monodentate PGM complexes with low and high-molecular-mass ammonium cations give satisfactory results in ion interaction HPLC on reversed phase silica in the presence of CH_3CN or CH_3OH modifiers. PGM chelates often show considerable shortcomings due to kinetic hindrance during their formation and must be formed prior to HPLC application. Capillary zone electrophoresis (CZE) brings some new aspects to the separation of PGMs in addition to increasing separation speed and miniaturization of the system. Both methods can be successfully used for the treatment of platinum anti-cancer drugs, their organic impurities, hydrolytic products or metabolites in body fluids. Representative examples are discussed in this paper.

Introduction

The determination of platinum group metals (PGMs), especially of platinum it self, has become an important task for industrial, environmental and biological samples. Some comprehensive reviews of the analytical chemistry of PGMs are now available [1–3]. Satisfactory results are obtained for the determination of PGMs by electrothermal AAS, ICP-AES or ICP-MS, but a sophisticated sample decomposition and separation or preconcentration of PGMs are usually obligatory prior to the determination [4]. HPLC and CZE may sometimes solve the problem of non-selectivity for PGMs at $\mu g\,mL^{-1}$ or sub$\mu g\,mL^{-1}$ levels but also can be used (a) to study complex equilibria of PGMs in solutions, particularly platinum (II) and platinum (IV) complexes, their decomposition products and metabolites in body fluids, (b) to identify platinum complexes in living objects, platinum anti-cancer drugs, their metabolites and decomposition products and (c) to differentiate between oxidation state of the same PGM.

The absence of simple hydrated ions in solution, the complicated equilibria with monodentate ligands, the kinetic inertia of their complexes in aqueous solutions and the existence of species with variable valency are typical for the PGMs [5–7]. The evaluation of PGM complexes is usually done spectrophotometrically or electrochemically, but on-line hyphenation with ICP-AES, ICP-MS or electrothermal AAS is more sensitive.

Normal phase HPLC has been used for the separation of neutral PGM chelates in the past. At present, RP-HPLC on chemically modified sorbent surfaces is predominant for neutral PGM chelates or charged complexes in the presence of ion pairing or ion interaction reagents. Ion exchange HPLC on silica based ion exchangers is also suitable for the preconcentration or partial separation of anionic inert PGM complexes at high or atmospheric pressure levels.

The interaction of PGM species with bare silica or chemically modified silica columns is a complicated phenomenon. The retention is controlled *inter alia* by (a) the stoichiometry and stability of the complex, (b) the structure of the ligand, (c) the kind and contents of the ion interaction reagent, (d) the organic modifier and the composition of the mobile phase (cf. [8–11]). Thus, the prediction of the retention of a particular PGM is questionable.

The migration of anionic inert PGM complexes or charged chelates in CZE has been carried out in fused silica capillaries whose surface is sometimes modified by

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cationic surfactants or in the presence of micelles.

The HPLC of some PGM species has already been reviewed [10, 12–15] but a critical evaluation of the present state of HPLC and CZE of PGMs is still desirable.

Ion Interaction RP HPLC of PGM Complexes with Monodentate Ligands

The ion pairing of inert anionic PGM halogenide, cyanide or thiocyanate complexes with organic cationic counter ions in solution is rather fast in contrast to chelate formation [16–18]. In spite of the ion associate formation in solution the dynamic ion interaction with the previously retained ion interaction reagent is the main process on hydrophobic silica columns so far as the sorbent surface has been saturated with the ion-interaction reagent. It is also assumed that the retention of the particular ion associate may appear under practical working conditions when competing excess perchlorate or halogenide ions are absent in solution [8, 16, 17, 19]. Non-specified hydrophobic interactions, proton-acceptor, dipole-dipole interactions and hydrogen bonding with the rest of the OH groups on the sorbent surface have also to be taken into consideration.

Halogenide Complexes of PGMs

Satisfactory results were obtained for PGM-bromide complexes in the presence of tetramethylammonium(TMA), tetrabutylammonium(TBA) halogenide, hydroxide or hexadecyltrimethylammonium bromide (CTMA) when octadecyl silica and 60% CH$_3$CN or 80% CH$_3$OH were used as stationary and mobile phases [16]. Solution with pH 3, 0.02 M NaBr and 0.002 M CTMA bromide were optimal (cf. Table I). While a proton-acceptor mechanism predominates with methanol, dipole-dipole interactions are expected with acetonitrile, which gives more symmetric peaks. The retention factors of PGM complexes on octadecyl silica increase with increasing concentration of the ion interaction reagent until some concentration maximum is reached, from which CTMA has the largest effect. In contrast, the retention factors of PGMs decrease with increasing volume fraction of CH$_3$CN in the mobile phase, whereas low bromide concentrations have a stabilizing effect on the retention. The sorbent surface was usually not fully saturated by the ion-interaction reagent so that in operation the retention mechanism may be more complicated.

Various low molecular and high molecular mass ion interaction reagents change the elution order for the PGMs in a number of ways (cf. Table I and Figure 1A for the use of CTMA bromide). Detection limits were 0.9 ng Pd, 6.7 ng Pt(II), 0.4 ng Pt(IV) or 4.3 ng Au(III) in 20 μL at 283–343 nm. Linear calibration plots from the peak heights were observed for $\leq 10\,\text{ng} \cdot 20\,\mu\text{L}^{-1}$. Fe(III), Al, Ca, Mg, Na, Cl, NO$_3^-$, SO$_4^{2-}$, do not interfere in 5000:1 excess [16]. The mobile phase CH$_3$CN–0.02 M phosphate with pH 7 (35:65) containing 0.05 M sodium bromide and 0.1 M TBA bromide was also suggested for the separation of bromide complexes of Rh(III), Pd(II) and Pt(II) on octadecyl silica [20, 21] but without significant advantage in comparison to previous conditions.

Thiocyanate Complexes of PGMs

PGM thiocyanate complexes are suitable for the RP-HPLC on octadecyl silica in the system containing CTMA bromide, sodium bromide and 60% CH$_3$CN at pH 2–4 as mobile phase. Their prior preparation from PGM chloride complexes in solution is, however, more difficult. The retention times for the PGM follows from Figure 1B but the separation of Pd and Pt or Pt(IV) from Pt(II) has practical significance only (cf. Table I). The detection limits are 0.1 ng Pt(IV) and 0.3 ng Pt(II) in 20 μL at 240–290 nm. Calibration plots from the peak heights are linear for less than $5\,\mu\text{g}\,\text{mL}^{-1}$ of PGM. No separation for Ir(III) and Ru(III) was observed under such conditions. Since thiocyanate complexes are more stable than PGM chloride or bromide complexes, bromide was used as competing ligand to enhance the elution of PGMs. An excess of Fe(III), Mg, Ca, Al, nitrate or sulphate or chloride does not interfere [17].

Cyanide Complexes of PGMs

The readily stable anionic cyanide complexes of PGM and Au(I) are suitable for the simultaneous determination of Au(I), Pd(II) or Pt(II) on cyanopropyl- or octadecylsilica in the presence of a number of common metal ions when aqueous CH$_3$CN and the ion interaction reagents TMA and TBA were used. The separation ability of metal cyano- complexes follows the stability and the charge of complexes but their retention capacity is also influenced by the amount of organic modifier, the concentration of ion interaction reagent, the excess of CN$^-$, pH and ionic strength of the mobile phase. According to a detailed study, dynamic or simple ion exchange prevail for sorbents saturated by the ion interaction reagent or in the presence of perchlorate as competing anion. In this case, the stationary phase was first equilibrated with the ion interaction reagent to minimize retention changes. Three different elution orders were observed for cyanide complexes by varying the concentration of perchlorate in the mobile phase but the sequence of PGM metal complexes remains constant [11] (cf. Table I).

The procedure is useful for the determination of traces of gold in the presence of common heavy metals after previous on-line preconcentration [22–24]. Similarly the ion associate of Pd(CN)$_4^{2-}$ with TBA butyrate could be readily separated from Ni(II), Au(I), Co(III), Cu(I), Ag(I) cyanide complexes with 28% CH$_3$CN at pH 7 (phosphate buffer) [15].

Thiourea Complexes with PGMs

Thiourea showed separation properties for some PGM when octadecyl silica and 50% CH$_3$CN containing 2 mM dodecylsulphate and 10 mM thiourea were used at pH 2.5. Cationic thiourea complexes of Pd(II), Pt(II) and Rh(III) previously formed in perchlorate medium after 60 min of heating on a water bath readily interact with dodecylsulphate. The retention factors increased in the following order: Pd(II) < Pt(II) < Rh(III). Several complexes of Pt(II) and Rh(III) are formed depending on the thiourea concentration. Double peaks were explained by the formation of various complexes [25]. Unfortunately, such procedures have little significance for the separation and determination of PGM in practice.

Ion Exchange HPLC of PGM Complexes with Monodentate Ligands

The separation of PGM chloride complexes has been carried out on silica-based

Table I. Ion Interaction RP-HPLC of representative PGM complexes on chemically modified silica.

PGM complexes	Ion-interaction agent	Chromatographic conditions	Elution order or retention factors	Reference
bromide	0.002 M CTMA bromide	octadecyl silica 60% CH_3CN, 0.05 M NaBr, pH 3	Rh(III) <Ir(IV) << Pd(II) < Pt(II) < < Os(IV) < Pt(IV) < Au(III) Ru(IV) moved with the solvent front	[16]
	0.002M CTMA bromide	octadecyl silica 80% CH_3OH, 0.02M NaBr, pH 3	Au(III) < Pt(IV) < Pd(II) < Pt(II)	[16]
	0.1 M TMA bromide	octadecyl silica 20–60% CH_3CN or CH_3OH, 0.02 M NaBr, pH 3	Pt(II) < Pt(IV) < Pd(II) < Au(III)	[16]
	0.1 M TBA hydroxide	octadecyl silica 45–60% CH_3CN or CH_3OH, 0.02 M NaBr, pH 3	Pt(II) < Pd(II) < Pt(IV) < Au(III)	[16]
thiocyanate	0.002 M CTMA bromide	octadecyl silica 60% CH_3CN, 0.05 M NaBr, pH 3	Rh(III) < Pd(II) < Os(IV) < Pt(II) < <Pt(IV)	[17]
	0.002 M CTMA bromide	Separon SGX AX 30–40% CH_3CN or 45% CH_3OH, 0.6–1 M $NaClO_4$, 0.01–0.05 M NaSCN	Rh(III) < Ru(IV) < Ir(III) < Pt(II) < < Pt(IV) < Pd(II)	[17]
cyanide	0.005 M TMA hydroxide	octadecyl silica 23% CH_3CN	Cu < Ag(I) < Fe(II) < Co(III) < Fe(III) < Au(I) < Pd(II) < Pt(II)	[22]
	0.005 M TMA hydroxide	cyanopropyl silica 8% CH_3CN	Co(III) < Cu(I) < Ag(I) < Ni(II) < Pd(II) < Au(I) < Pt(II)	[22]
	0.005 M TBA chloride	octadecyl silica 32% CH_3CN, CN excess, pH 7	Pd(II) < Pt(II) < Au(I)	[23, 24]
	0.006 M TBA hydroxide	octadecyl silica 25% CH_3CN, 2.34 mM $NaClO_4$	Mo(IV) < Cu(I) < Co(III) < Fe(III) < Ni^{2+} < < Cr(III) < Pd(II) < Pt(II) < Au(I)	[11]
	0.001 M TBA butyrate	octadecyl silica 28% CH_3CN 0.001 M CN , pH 9.5	Cu(I) < Ni < Au(I) < Pd(II) < Co(III)	[15]

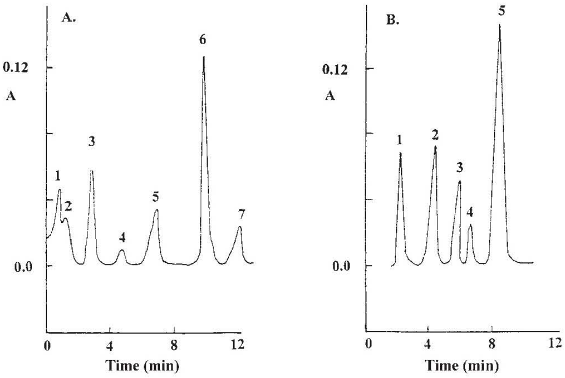


Figure 1. A. Separation of bromide complexes from 60% CH_3CN with 0.002 M CTMA, 0.05 M NaBr, pH 3 on Separon SGX RPS, column 150 × 3 mm, 200 ng of metal in 20 µL. Detection at 240 nm. The ion-interaction RP-HPLC and the ion-pair formation in solution influence commonly the retention of PGM species on the column. **1** = Rh(III) + Ir(III), **2** = Ru(III), **3** = Pd(II), **4** = Pt(II), **5** = Os(IV), **6** = Pt(IV), **7** = Au(III). **B.** Separation of SCN complexes from 60% CH_3CN with 0.002 M CTMA, 0.005 M NaSCN + 0.05 M NaBr, pH 3. Detection at 240–290 nm. **1** = Ru(III) + Ir(III) + Rh(III), **2** = Pd(II), **3** = Os(IV), **4** = Pt(II), **5** = Pt(IV); Compiled from the paper of Doležal, J.; Sommer L. *Collect. Czech. Chem. Commun.* **1997**, *62*, 1029–1042 and not published data with permission.

anion exchanger using aqueous CH_3CN with various concentrations of sodium perchlorate. A successive elution of Au(III), Pt(IV), Ir(III), Rh(III), Ru(III) and Os(IV) followed with 30% CH_3CN containing 0.08–0.12 M sodium perchlorate but only Os(IV) and Ir(IV) and Pt(IV) gave consistent peaks. Detection limits were between 2–10 ng mL^{-1} at 240 nm [26]. Mixed halogenide complexes of Os(IV) were surprisingly separated on anion exchanger under gradient elution with perchloric acid [27]. $PtCl_4^{2-}$, $PtCl_6^{2-}$ and their hydrolytic products were successively separated by a mixture of 0.3 M $NaClO_4$–48 mM HCl with pH 1.3 on an Ion Pac AG5 and Ion Pac AS5 two column system [28].

A satisfactory separation of PGM also resulted from thiocyanate complexes on anion exchanger Separon SGX AX by subsequent elution with 30–40% CH_3CN or 45% CH_3OH containing 0.6–1 M $NaClO_4$ and 0.01–0.05 M NaSCN at pH 2.5. The SCN^- in the mobile phase hinders the partial hydrolysis to hydroxothiocyanate complexes. Linear calibration plots were obtained for 10 µg Pt(IV), Pt(II) or Pd(II) and detection limits 10.7 ng Pt(II), 6.9 ng Pt(IV) and 6.7 ng Pd(II) in 20 µL [17].

The separation of Rh(III), Pd(II) and Pt(IV) in the form of chloride complexes was also realized by medium pressure LC on macroreticular hydroxyethylmethacrylate-ethylenedimethacrylate copolymer containing diethylaminoethyl groups (Spherone DEAE). The order of elution times was Rh(III) < Pd(II) < Pt(IV) in 5 M HCl containing 0.5 M $NaClO_4$. The retention capacity for Pt (IV) is increased by high-molecular-mass octadecyl amine or benzyldodecyldimethyl-ammonium bromide [29].

HPLC of PGM Chelates

The formation of PGM chelates, especially of Pt(IV), Pt(II), Rh(III), Ir(III), Os(IV, VI), Ru(IV, VI) is kinetically hin-

Table II. The use of selected N-Heterocyclic azodyes for the HPLC of PGMs.

Reagent	Chromatographic conditions (sorbents, mobile phases)	Elution order of retention factors	Ref.
1-(2-Pyridylazo)-2-naphtol[1] (2-PAN)	normal phase HPLC: Silasorb 600 Benzene-2-propanol (9:1, 1:1), acetone-$CHCl_3$ or acetone	Pt(II) < Rh(III) (1.peak) < Pd(II) (1.peak) < Pd(II)(2.peak) < Rh(III)(2.peak) < R < Cu(II) < Co(III) Ni(II) < Pd(II) < Cu(II) < Co(III)	[12, 40, 41, 43]
	RP-HPLC: Spherisorb CN, silanized silica (silica RP2, RP8, RP18) at pH 5 CH_3CN–0,1 M–$NaClO_4$ (4:6) or dioxane-CH_3CN–0,1 M–$NaClO_4$ (20:30:50) at pH 4–6 CH_3CN-H_2O-citrate buffer (80:18:2)	Pd(II) < Pt(II) < Rh(III)	[13, 44]
4-(2-Pyridylazo)resorcinol (PAR)	RP-HPLC: Octadecylsilica Yanapak ODS-T 30% CH_3CN, NaCl, EDTA, acetate buffer (pH 5,6), 0,01 M-TBA bromide	Separation of Pd(II), Pt(II)	[93]
4-(5-Nitro-2-pyridylazo) resorcinol	RP-HPLC: CH_3OH-ethylacetate-H_2O (50:10:40) acetate buffer with pH 4, TBA bromide and EDTA	Rh(III) < R < Ru(IV) < Pd(II) < Pt(II)	[94]
2-(5-Bromo-2-pyridylazo-5-(N-propyl, N-sulphopropylamino) phenol (5-Br-PAPS)	RP-HPLC: LiChrosorb RP-18 65% CH_3OH containing 7.10 ^{4} M butylammonium chloride, 1.10 ^{4} M CDTA and 0,01 M NH_4^+ acetate (pH 4.0)	Rh(III) < Pd(II) < R < Pt(II)	[45]
1-(2-Thiazolylazo)-2-naphtol (2-TAN)[1]	RP-HPLC: Octadecylsilica CH_3CN-acetate buffer (pH 4.4)-0,1 M NH_4SCN (80:15:5)	Separation of Pd(II) < Pt(II) < Rh(III) < < Ru(IV) < Ir(III)	[95]
	normal phase HPLC: Silasorb 600 Toluen-aceton (93:7) or dichloroethane-ethanol (93:7)	Separation of Pd(II), Rh(III)	[96]
1-(2-Thiazolylazo)-2-naphtol-3,6-disulphonic acid[1]	RP-HPLC: Nucleosil C18, Separon C18 60% CH_3CN containing 0,01 M CTMA bromide, phosphate or acetate buffers (pH 6.9)	Co(III) (Fe(II)) < R < Cu(II) < Pd(II) < < Ni(II)	[97]
4-(2-Thiazolylazo) resorcinol[1]	RP-HPLC: Silicagel C18 30–40% CH_3CN containing $\leq$ 0,05 M TBA bromide, acetate buffer (pH 5.1)	Rh(III) < Ru(IV) < Os(IV), Cu Cu < Ru(IV) < Co < Rh(III) < Os(IV)	[98, 99]
2-(2-Thiazolylazo)-5-diethyl-aminophenol (TADAP)[1]	RP-HPLC: Silicagel C18 50% CH_3CN, 25% acetate buffer (pH 5.1) and 3.5 mM CTMA bromide	Rh(III) < Pt(II) < Pd(II) < R < Ru(IV)	[100]
2-(6-Methyl-2-benzothiazolyl-azo)-5-diethylaminophenol (MBTAE)[1]	RP-HPLC: Silica C8, C18 CH_3OH-H_2O (153:47) or 73% CH_3OH and acetate buffer (pH 6) or CH_3OH-n-butanol-H_2O (75:5:25) in the presence of 5 mM ethylendiamindiacetic acid diethylacetate (pH 4.5)	Pt(II) < Rh(III) < Pd(II) < R < Ru(IV) < < Os(IV)	[101–104]

R – reagent peak; [1] – suitable for the determination of PGMs in the presence of limited excess of common heavy metals.

dered and only proceeds slowly under extended heating or boiling. Perchloric acid or sulphuric acid is a suitable medium in the presence of sodium acetate as a coordination catalyst but 20–40% dimethylformamide or dimethylsulfoxide in a slightly acid medium can also be used. PGM-halogenide or thiocyanate often cannot be transformed to chelates or interfere strongly (cf. also [30, 31]). The PGM chelates often show considerable absorption coefficients in the visible or UV range and are detected spectrophotometrically. Normal phase HPLC or RP-HPLC have been used for electroneutral, sufficiently stable and coordination-saturated PGM chelates. Charged chelates are separated by RP-HPLC in the presence of various ion interaction reagents. Various retention models come into consideration on the silanized silica [8, 9, 15, 32, 33] but the retention of the anionic metal chelates after previous dynamic saturation of the sorbent surface with the ion interaction reagent is preferred. Competing inorganic anions in excess in solution may cause the usual ion exchange [10, 15].

For normal-phase HPLC, there is an apparent relation between the electronegativity of the chelated metal and the PGM chelate retention on bare silica columns. With increasing electron density on the ligand donor atoms the adsorption strength of the metal chelate increases. Thus, the retention factors of metal chelates correlate with the decrease in chelate stability. The strength of the hydrogene bonding between the silica gel-OH groups and the oxygen-donor atom belonging to the ligands is of considerable importance (cf. also [12]).

N-Heterocyclic Azo-dyes

Russian authors, in particular, have paid a great attention to the application of N-heterocyclic hydroxy azo dyes for the chromatography of metals including PGM (cf. [10, 12, 13, 15, 34]). N-Heterocyclic azo dyes suitable for the separation of PGMs by HPLC, some of them in the presence of common metal ions, are compiled in Table II. With the exception of 1-(2-pyridylazo-2-naphtol) (2-PAN) N-pyridylazodyes have little significance for the HPLC of PGMs on bare and chemically modified silica. This comes *inter alia* from the complicated complex equilibria of these reagents and kinetic hindrance during PGM complex formation. Except for Pd (II) [35, 36] and Pt(II) [37–39], detailed information about equilibria, complex stoichiometry and stability are missing.

The charge-free 2-PAN chelates have frequently been used in combination with normal phase HPLC and non-polar mobile phases after prior extraction into $CHCl_3$ or isopentanol. The high adsorptive strength of the PGM chelates on bare

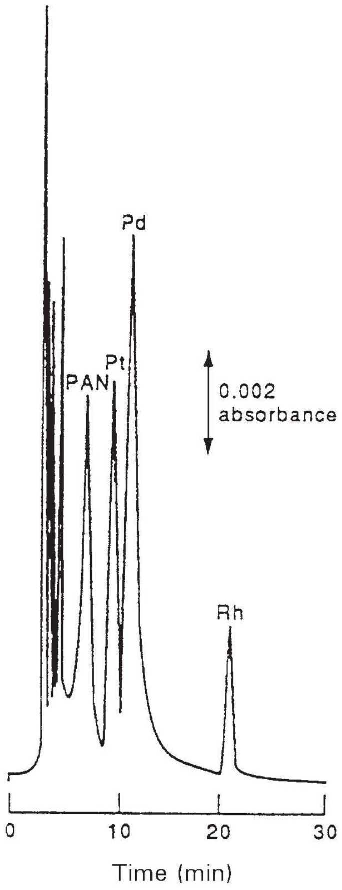


Figure 2. Separation of Pd(II), Pt(II) and Rh(III) chelates with 1-(2-pyridylazo)-2-naphthol from 40% CH_3CN containing 0.1 M sodium perchlorate at pH 4 on Spherisorb CN. Detection at 440 nm. The retention of PGM results from the complicated complex equilibria in solution and the mixed retention mechanism on the sorbent. Reproduced from the paper of Timerbaev, A.R.; Petrukhin, O.M.; Alimarin, I.P.; Bol'shova, T.A. *Talanta* **1991**, *38*, 467–476 with permission.

silica with long elution times is a disadvantage [40, 41]. No considerable improvement was, observed for RP-HPLC of 2-PAN chelates on silanized silica with CH_3CN or dioxane mixtures containing sodium perchlorate [13, 44] (cf. Figure 2). The detection limit for PGMs can be improved by the previous extraction-chromatographic preconcentration of 2-PAN chelates into 2-pentanol and $CHCl_3$ on polytetra-fluoroethylene [12, 40–43].

In contrast to N-pyridylazo dyes, N-thiazolylazo dyes were frequently used for the separation of PGMs by RP-HPLC on octadecyl- or octyl silica in the presence of ion pairing reagents. A number of N-thiazolylazo complexes are less stable than those of N-pyridylazo complexes decompose on columns, do not give peaks and do not interfere with the HPLC of PGMs. Figure 3 is shown as example.

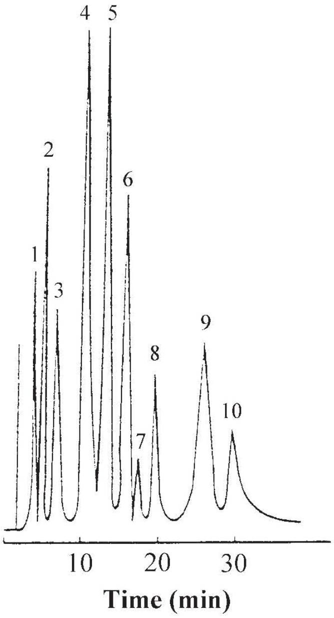


Figure 3. Separation of metal chelates by RP-HPLC with 2-(6-methyl-2-benzothiazolylazo)-5-diethylaminophenol on octyl silica from 76% CH_3OH containing acetate buffer (pH 5). **1** = Rh(III) + Ir(III), **2** = Cu, **3** = Pt(II), **4** = reagent, **5** = Ni, **6** = reagent, **7** and **8** = Ru(III, IV?), **9** = Os(IV), **10** = Co; Reproduced from the paper of Liu, Q.P.; Zhao, T.; Liu, J.C.; Cheng, J.K. *Mikrochim. Acta* **1996**, *122*, 27–33 with permission.

Dithiocarbamates

The chelates of Pt(II), Pd(II), Rh(III), Ru(III) and Ir(III) with diethyldithio-carbamate in 70% CH_3CN at pH 5 or pure CH_3CN are retained on octadecyl silica and detected in the UV, but the separation is not perfect. The procedure can only be used for the determination of Pd(II) and Rh(III). The neutral PGM chelates are previously formed at room temperature (for Pd(II) and Ru(III)) or under heating, and salted out with saturated sodium chloride solution into CH_3CN at pH 1.7–11.7 which is rather inconvenient for practical use [45–47].

8-Hydroxyquinoline

8-Hydroxyquinoline reacts with Pd(II), Rh(III), Ir(IV), Ru(III) and Os(IV) in acetate buffer at 90 °C. The PGM chelates are extracted into $CHCl_3$ prior to HPLC and separated on bare silica (Silasorb 600) with 1,2-dichlorethane-2-propanol (97:3) or (98:2). The retention factors follow the order: Pt(II) < Pd(II) < Os(III) < Ru(III) < Ir(IV)< Rh(IV). Detection limits (ng in 5μL) are: Pd(II) 0.3, Pt(II) 1.0, Rh(III) 1.0, Ir(IV) 5.0, Ru(III) 1.5 and Os(IV) 25 at 254 nm [48]. Octyl silica with CH_3OH-0.03 M acetate buffer (pH 4,6)- $CHCl_3$ (23:12:5) containing 0.25 mM 8-hydroxyquinoline can also be used for the separation of Ru(III), Rh(III) and Ir(IV) chelates [49].

Chelones

Some anionic 1:1 PGM-chelates of iminodiacetic (IDA), nitrilotriacetic (NTA), ethylendiamine tetraacetic (EDTA) and cyclohexanediamine tetraacetic (CDTA) acids in the presence of TEA, TBA or CTMA bromides have been suggested for the RP-HPLC separation of PGM on octadecylsilica but the results are not sufficiently promising [50–52]. Nevertheless, the separation of anionic PGM chelates with IDA has been recommended in binary mixtures from buffered aqueous solutions (pH 3.8–6.8) or aqueous CH_3CN. The CDTA chelates seem to be more suitable for the separation of Pd(II) from other PGMs and common transitory elements in model solutions [51]. Detailed studies of the interaction with octadecylsilica proved both, the adsorption of ion pairs only or the dynamic ion exchange for different PGM-chelones [52].

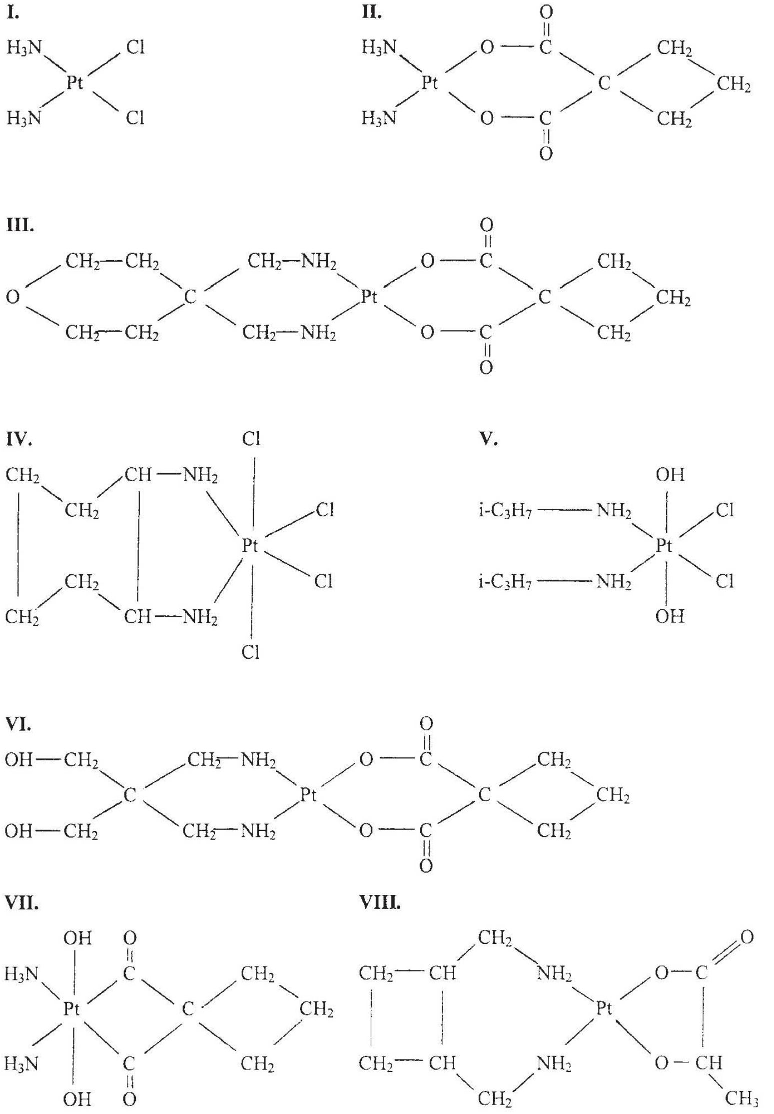
Other Chelating Agents

Pd(II) gives complexes with 5-sulphosalicylic acid at pH 2.7 unlike Pt(IV) and Ir(IV). This can be used for the separation of the above metals on the anion exchanger Spheron 1000 at pH 2.7. Rh(III) does not interfere [53].

Acetylacetone and benzoylacetone were reported for chromatographic separation of Rh(III), Ru(III), Pt(II) [54], benzothiazolthiol for Rh(III) and Ir(III) [55], 1-hydroxydihydropyridine-2-thione for Pt(II), Pd(II), Rh(III), Ir(IV) [27, 56, 57], tetradentate Schiff bases [58] and dialkyldithiophosphonic and dithiophosphinic acids for Pd(II) [59], but their use for solving practical analytical problems is rather limited.

HPLC of Platinum Anti-cancer Drugs, their Derivatives and Speciations

Table III. Survey of selected anti-cancer drugs followed chromatographically



I. Cisplatin (Platinol, Platidiam) cis-diaminodichloro platinum (II) **II. Carboplatin** cis(diamin-1,1-cyclobutane-1,1-dicarboxylato) platinum (II) **III. Zeniplatin** 2,2-bis(aminomethyl)-1,3-propanediol-N,N')(cyclobutane-1,1-dicarboxylato-O,O') platinum (II) **IV. Tetraplatin** tetrachloro(trans-1,2-diaminocyclohexan) platinum (IV) **V. Iproplatin** cis-dichloro-trans-dihydroxyisopropylamine platinum (IV) **VI. Enloplatin** (cyclobutane-1,1-dicarboxylato-O,O')(tetrahydro-4H-pyran-4,4-dimethanamine-N,N') platinum (II) **VII. Oxo-carboplatin** dihydroxoamine (1,1-cyclobutane-1,1-dicarboxylato) platinum IV) **VIII. Lobaplatin** 1,2-diaminomethylcyclobutane platinum (II) lactate

A comprehensive review of the clinical, pharmacokinetic and analytical aspects of cancer therapy with some platinum compounds has been published and ICP-AES with electrothermal vaporization was recommended for the determination of platinum in clinical microsamples [60]. Plasma ultrafiltrate, urine or tissue samples are the usual materials for testing for these drugs during therapy. From the platinum(II) complexes cis-diammindichloroplatinum (Cisplatin), cis-diammin-1,1-cyclobutandicarboxylate- platinum (Carboplatin), cis-diisopropylaminodihydroxo-dichloroplatinum (Iproplatin), several other Pt(II) complex analogues and one Pt(IV) species are of special interest for cancer therapy [53, 61–65] (cf. Table III). The original drug and its metabolites together with hydrolytic products and impurities in the drugs have to be evaluated as well [cf. 66]. Moreover, free platinum and various platinum(II) species formed by biotransformation or bound to proteins are distinguished after ultrafiltration.

The interaction of Cisplatin with DNA, nucleotides or methionine was monitored on silica dynamically coated with hexadecyltrimethylammonium bromide using mobile phases containing phosphate buffer with pH 7.0 or octadecyl silica in ion-interaction mode with alkylsulphonates. In such case, the mobile phase contained phosphate buffer with pH 2.1, 10–12% CH_3CN and 50 mM hexanesulphonate. The species were detected spectrophotometrically at 254 or 280 nm [67].

Similarly, Cisplatin and its hydrolytic and decomposition products are separated on octadecylsilica (Silasorb SPH C 18) coated with octanesulphonate using a mobile phase containing octane sulphonate and dihydrogenephosphate with pH 4.3 and variable ionic strength gradient [68]. The separation of cationic hydrolytic products from the parent Cisplatin was successfully achieved on sorbent modified by solutions containing 5 mM heptane or hexane sulphonate and 10 mM sodium acetate with pH 4.60. The separation of platinum(II)- and platinum(IV) complexes can also be realized in this way [69].

The separation of hydrolytic products, Cisplatin and the complex of Pt(II) with methionine can also be carried out on octadecylsilica with a mobile phase containing dihydrogenphosphate at pH 2–4, 1 mM octane sulphonate and 5–15% CH_3CN or 5% propane-2-ol. The above complexes were detected spectrophotometrically or by ICP-AES interfacing the chromatograph on-line with the cross-flow nebulizer of the ICP spectrometer containing a PTFE capillary [70].

Silica-NH_2 (LiChrosorb-NH_2) is suitable for the separation of Cisplatin from Transplatin complexes with aqueous CH_3CN as mobile phase. Cisplatin shows stronger retention on the amino groups of the sorbent than the trans derivative [71]. Both, octadecyl silica and octyl silica are also suitable sorbents for distinguishing cis- and trans-platinum(II)complexes when water is used as the mobile phase. Excess of chloride or mannitol does not interfere [72].

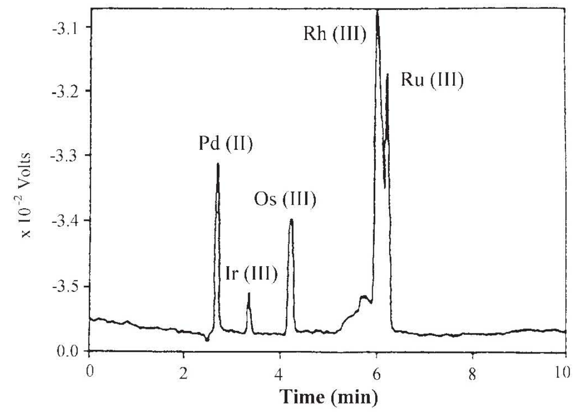


Figure 4. Separation of PGMs by CZE from chloride complexes in the presence of Cu(II), Ni(II), Fe(II), Co(II). The carrier electrolyte contains 50 mM HCl – KCl and 0.2mM cetyltrimethyl-ammonium bromide at pH 3. Detection at 214 nm. Reproduced from the paper of Zhang, W.H.; Li, J.; Hu, Z.D. *J. Chromatogr. A* **1995**, *707*, 242–246 with permission.

Iproplatin was monitored as a cationic species by ion-interaction RP-HPLC. The optimal mobile phase was 20% CH_3OH and 10 mM dihydrogenphosphate containing various 1 mM alkylsulphonates at pH 3.5 [62].

Cisplatin, Transplatin, Carboplatin and related neutral, anionic or cationic species of Pt(II) were studied on octadecylsilica dynamically modified with a mixture of cationic and anionic amphiphilic modifiers. Gradient elution with mobile phases containing 0–6 mM TBA hydrogenesulphate and 0–4 mM octane sulphonate (pH 5.9) was successfully used [73].

The purity of platinum cytostatics and the degradation of Carboplatin to the more toxic Cisplatin can be tested on octadecyl silica with water as the mobile phase only. The cytostatics were preseparated from sera on an octadecyl silica microcolumn and eluted successively with a mixture of CH_3OH- H_2O (1:1) and methanol [74]. LiChrosorb NH_2 with 70% CH_3CN at pH 4.5–4.7 is also suitable for the separation of Cisplatin and its metabolite trans-dihydroxo diammin dichloro platinum(IV). Some more complicated complex pH-dependent equilibria were indicated from the family of peaks in the chromatogram [71, 75]. A Hypersil Phenyl column combined with a short guard column and 75% CH_3CN gives similar results [61, 66].

More sensitive detection, e. g. by ICP-AES can be used with RP-HPLC for monitoring platinum species from antitumor drugs in living objects during cancer therapy [76]. The highly sensitive hyphenation techniques of HPLC-ICP-MS, HPLC-ICP-AES, or HPLC with voltamperometric reductive or oxidative detection of Cisplatin and derivatives have been used successfully tested [63]. Reductive electrochemical detection in combination with ET- AAS was tested for the detection of various platinum(II) anti-cancer drugs after separation on octadecyl and octyl silica (Zorbax C 8 and Zorbax ODS). An off-line evaluation of platinum by AAS was used after the retention of Cisplatin from urine on octadecylsilica (Hypersil ODS) covered with hexadecyltrimethylammonium bromide. Elution followed with 0.01 M citrate (pH 7.0) containing 1.10^{-4} M surfactant [77]. A simple post-column reaction of a number of Pt(II) complexes was developed during anti-cancer treatment after separation on octadecylsilica covered with 10^{-4} M hexadecyltrimethylammonium bromide and 10 mM citrate (pH 5.25) [53]. Various metabolites of Cisplatin traced with radioactive ^{195}Pt can also be detected radiochemically in plasma ultrafiltrates after separation on octadecylsilica (Spherisorb ODS) when using 5 mM sodium dodecylsulphate and sodium dihydrogenphosphate (pH 2.6) or 25% 2-propanol with dihydrogenphosphate (pH 2.6) as mobile phases [78, 79].

Capillary Zone Electrophoresis (CZE) of PGMs

CZE of PGM Chloride Complexes

The CZE of Pt(IV) and Pd(II) in the form of chloride complexes has been carried out in a bare fused silica capillary with two carrier electrolytes: (a) 0.1 M HCl and 0.4 M NaCl at pH 2, or (b) acetate buffer with pH 5.5 containing 0.1 M tetradecyltrimethyl-ammonium bromide for reducing the electroosmotic flow. Two peaks appeared in fresh 0,1 M HCl solutions containing Pt(IV) and Pd(II), which corresponded with the highest chloride complexes of these metals, e. g. $PtCl_6^{2-}$ and $PtCl_4^{2-}$. After 60 min an additional peak belonging to $PtCl_5(H_2O)$ appeared. The evaluation of peaks was done spectrophotometrically at 225 or 262 nm. The plots of peak height or surface area were linear for 5–40 µg mL^{-1} Pt or Pd. In contrast to Pt(IV)Cl_6^{2-}, Pt(II)Cl_4^{2-} hydrolyzes easily in slightly acid solutions which causes a reproducible peak immediately during the electrophoresis [80].

Pd(II) can be easily separated from Rh(III), Ru(III), Os(III) and Ir(III) by electromigration in a chloride medium (cf. Figure 4). The electrophoretic mobility decreases with increasing pH because of complex hydrolysis. pH 3 is optimal for carrier electrolytes containing diluted HCl and KCl or NH_4Cl. The increasing concentration of carrier electrolyte reduces both the electrophoretic and electroosmotic mobilities of PGMs. In the presence of 0.2 mM CTMA bromide the electroosmotic flow changes direction. Various common metal ions do not interfere with Pd(II) in the presence of excess chloride [81].

A similar carrier electrolyte with pH 3–4 is suitable for the separation of PGM in a heated capillary. A partial dissociation of the highest chloride complexes to lower ones in solution was, however, observed which may influence the migration of Pd(II). The migrations times follows the order: Pt(II) < Os(IV) < Pt(IV) < Ir(III) < Pd(II) < Rh(III) [82] (cf. Figure 5). No effect of CTMA bromide was observed by these authors in contrast to the results of other workers [81].

A good separation of chloro and chloro hydroxy complexes of noble metals was proved in diluted HCl with pH 2.7 with migration times Os(IV) < Pt(IV) (1.peak) < Rh(III) < Pd(II) < Au(III) < Pt(IV) (2.peak) < Ru(III). The detection was again carried out spectrophotometrically at 214 or 254 nm [83].

CZE of PGM Thiocyanate Complexes

The separation of Pt(IV), Pt(II) and Pd(II) by the CZE of unknown thiocyanate complexes in an uncoated silica capillary has little advantage over other procedures. The 0.1 M KSCN adjusted to pH 3 by perchloric acid is the optimum carrier electrolyte. In such cases the migration times followed the order Pd(II) < Pt(IV) < Pt(II) and peaks were evaluated spectrophotometrically at 295 nm [84].

CZE of Cyanide Complexes

Cyanide complexes at pH 9.0–9.5 (phosphate buffer) have been recommended for the separation of Pd(II) from a number of common metals. The peaks were evaluated spectrophotometrically at 214 nm. The decomposition of some cyanide complexes during the migration is prevented by a small excess of CN^- [85]. A detailed study of cyanide complexes of different stability was carried out in phosphate-triethanolamine buffer with pH 8.3. 0.1–0.8 mM hexane-1,6-bis(trimethylammonium) bromide influenced the electroosmotic flow, decreased the analysis time and improved the shape of the peaks. In addition, the separation of Pd(II) and Pt(II) cyanide complexes from Au(I) and a number of heavy common ions has been improved [86].

Traces of CN^- as its anionic complexes could be determined after on-line preconcentration with a liquid membrane containing methyltrioctylammonium chloride in dibuthylether. The final CZE was performed off-line in a phosphate-triethanolamine buffer at pH 8.5 in the presence of hexamethonium bromide and sodium perchlorate. Pd(II) and Pt(II) were separated from Ag(I), Au(I), Cu(I), Cr(III), Co(III), Fe(II), Fe(III) cyanide complexes [87].

The metal cyanide complexes were also suggested as basis for the CZE determination of PGM in automobile catalytic converters after previous leaching the sample with alkaline cyanide solution in an autoclave and subsequent retention of PGMs on activated charcoal. The recommended carrier electrolyte was a hydrogenephosphate buffer with pH 11 containing 1.2 mM TBA bromide, 3 mM NaCN, 40 µM tetradecyltrimethylammonium bromide and 100 mM NaCl. The peaks of Pt(II) and Pd(II) detected at 208 nm were readily separated from those of common ions but Rh(III) could not be determined [88].

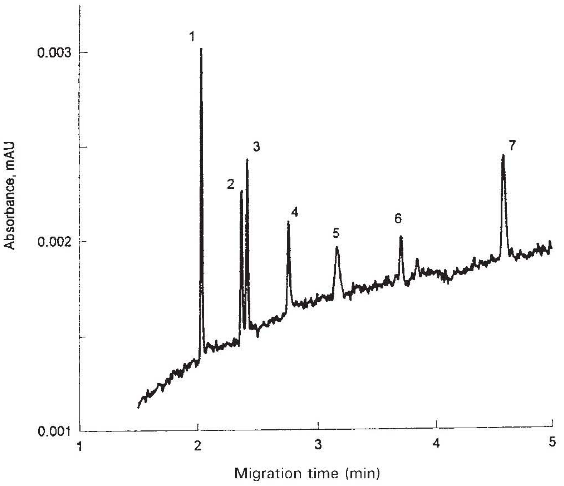


Figure 5. Separation of PGMs by CZE as chloride complexes. Carrier electrolyte was 60 mM KCl (pH 3.1), temperature 55 °C. Input Voltage −11 kV, detection at 214 nm. **1** = Pt(II), **2** = Os(IV), **3** = Pt(IV) (hydrolysis product), **4** = Ir(III), **5** = Pd(II), **6** = Pt(IV), **7** = Rh(III); Reproduced from the paper of Pirogov, A.V.; Havel, J. *J. Chromatogr. A* **1997**, *772*, 347–355 with permission.

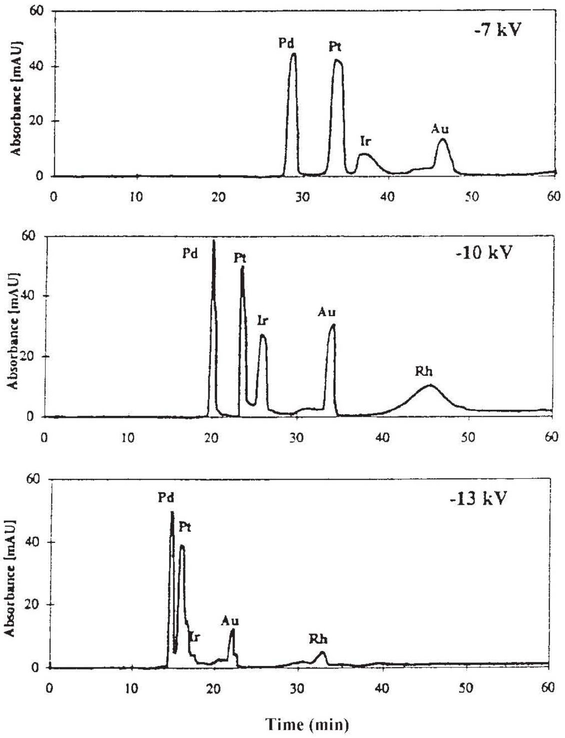


Figure 6. Effect of applied input voltage in the separation of PGMs by CZE as bromide complexes. Carrier electrolyte was sodium bromide, sodium acetate and $HClO_4$ (pH 3) in unmodified capillary. Reproduced from the paper of Mojski, M.; Gluch, I.; Obarski, N. *Chem. Anal. (Warsaw)* **1997**, *42*, 825–835 with permission.

CZE of PGM Bromide Complexes

Anionic bromide complexes of PGMs are a suitable medium for CZE in a bare silica capillary. The recommended carrier electrolyte contains 50 mM sodium acetate and 50 mM sodium bromide at pH 3. The migration times for PGM followed the order: Rh(III) > Au(III) > Ir(IV) > Pt(IV) > Pd(II) but is influenced by the input voltage used (cf. Figure 6). The peaks areas were quantified at 235 nm [26].

Separation of Thiourea Complexes

The cationic PGM complexes with thiourea can also be used for the separation in 20 mM $NaClO_4$ and 1 mM thiourea at pH 2.5 as carrier electrolyte. The separation is only effective for binary mixtures Rh(III)-Pd(II) and Rh(III)-Pt(IV) but of low practical significance [25].

CZE-ICP-MS of PGM Complexes

Nowadays, the on-line hyphenation of CZE with ICP-MS is common. A commercial slightly adapted interface is used with a home made nebulizer. The separation of metal chloride complexes was first obtained by CZE in a phosphate carrier electrolyte; ICP-MS ensured platinum detection with a low detection limit ($\sim 1\ \mu g\ L^{-1}$). The procedure was compared with a variant of RP-HPLC-ICP-MS and both applied for aqueous extracts from platinum-contamined soil [89–91].

CZE of Platinum Drugs

Some neutral anti-tumor platinum(II) drugs such as Cisplatin, Carboplatin and Lobaplatin (cf. Table III) and their positively charged hydrolysis products can be separated in one run by micellar electrokinetic chromatography in aqueous solutions containing dodecylsulphate. The optimal carrier electrolyte contained 80 mM sodium dodecylsulphate, 50 mM phosphate and 25 mM borate buffer (pH 7.0). Neutral complexes were separated from their hydrolysis products by the micellar effect. In this case a higher tendency toward hydrolysis was observed for Carboplatin and Lobaplatin than for Cisplatin in the presence of chloride excess [92]. Such treatment is preferred to the HPLC applied earlier [68].

Conclusion

HPLC is readily applicable for the separation and determination of various PGM species in pure solution or in the presence of a limited excess of common metal ions. Detection limits are in $\mu g\ mL^{-1}$ or sub-$\mu g\ mL^{-1}$ levels when spectrophotometric detection is used. The limit of detection can be improved when on-line preconcentration is used with microcolumns.

Ion-interaction RP-HPLC on chemically modified silica in the presence of high molecular mass cationic ion-interaction reagent is suitable for the separation of PGMs in the form of monodentate halogenide or thiocyanate complexes; low molecular mass reagents are recommended for cyanide complexes. The retention factors and the shape of the chromatographic peaks for particular PGMs is, however, considerably influenced by the organic modifier, the ion-interaction reagent, the ionic strength and the overall composition of the mobile phase.

Ion exchange chromatography of anionic monodentate PGM complexes on anion exchangers based on chemically modified silica or macroreticular polymers may also be suitable for the preconcentration and separation of PGM.

The formation of PGM-chelates from halogenide complexes and organic ligands prior the HPLC is kinetically hindered. PGM halogenide complexes have to be previously transformed to perchlorates or sulphates or solutions containing dimethylformamide or dimethylsulfoxide are used. RP-HPLC on hydrophobic chemically modified silica in the presence of ion interaction reagent and CH_3OH or CH_3CN modifiers is used with advantage for PGM of charged chelates. The composition and properties of the buffered mobile phase as well as the kind and amount of the interaction reagent determine the retention factors of PGM chelates with the particular reagent. Peaks of the chelating agents may interfere when spectrophotometric detection is used.

RP-HPLC is most successful for the separation and determination of Pd(II), Pt(II), Pt(IV), Rh(III), Os(IV) and Ir(IV) in mixtures where a limited excess of common metal ions does not interfere.

HPLC has special advantage for the determination of anti-cancer drugs based on platinum (II), their metabolites in body fluids and for the evaluation of hydrolysed species and complex impurities in therapeutically used platinum complexes. Satisfactory results have been obtained by HPLC during studies of platinum interaction with living objects or DNA components in cells or membranes.

The speed of analysis and the high resolution capacity of CZE are its advantages over HPLC for the separation and determination of PGMs in mixtures. Determining optimal separation conditions and finding the best peak shapes for quantification can be a tedious process in the CZE of PGMs. PGM chloride complexes are, however, rather stable and kinetically inert in acid solutions, so that acid carrier electrolytes can be used for the electromigration where the dissociation of silanol groups from the silica capillary is suppressed and the electroosmotic flow is minimized. In contrast to HPLC some lower PGM-halogenide complexes or chloro-hydroxy complexes become evident during the fast migration process. This fact may complicate the resulting electrophoreogram and contributes to artefacts making quantitation difficult. The effective mobilities and the position of the peaks of stable and inert PGM complexes depend *inter alia* on the effective charge, the stoichiometry of the complex and the mass and radius of the central metal ion. In contrast, differences in stability constants for complexes of the particular PGM with the same stoichiometry and charge, little influence the effective mobility. Similarly the carrier electrolyte buffered to the appropriate pH has usually little influence on the electrophoretic mobility of the PGM species unless pairing by counter-ions or mixed species formation takes place. The quantification of peaks is often difficult or complicated by peak deformations and high background level [82]. The sample stacking observed during the migration of PGM-chloride complexes with a ligand excess such as chloride in the carrier electrolyte, increases the peak height and improves the sharpness of the peak for better evaluation [81].

The use of CZE for the identification of platinum(II) complexes of various structure and effective charge but also for tests of purity, decomposition products and metabolites of anti-cancer drugs has a promising future.

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References

[1] Biu Qu, Y. *Analyst* **1996**, *121*, 139–161.
[2] Balcerzak, M. *Analyst* **1997**, *122*, 67R–74R.

[3] Pyrzynska, K. *Talanta* **1998**, *47*, 841–848.

[4] Vlašánková, R.; Sommer, L.; *Chem. Pap.* **1999**, *53*, 200–209.

[5] Ginzburg, S.I.; Yezerskaya, N.A. and Editors *Analiticheskaya Khimia Platinovych Metallov*, Nauka, Moskva, **1972**, p. 45–132.

[6] Smith, R.M.; Martell, A.E. *Critical Stability Constants*, 4, Plenum Press, New York, **1976**, p. 107.

[7] *Stability Constants of Metal- Ion Complexes*, Part A, Inorganic Ligands (compiled by E. Hoegfeldt), Pergamon Press, Oxford, **1982**.

[8] Timerbaev, A.R.; Petrukhin, O.M.; Orlov, V.I.; Aratskova, A.A. *J. Liq. Chromatogr.* **1992**, *15*, 1443–1461.

[9] Timerbaev, A.R.; Petrukhin, O.M. *Zh. Anal. Khim* **1991**, *46*, 213–224.

[10] Timerbaev, A.R.; Petrukhin, O.M.; Alimarin, I.P.; Bol'shova, T.A.; *Talanta* **1991**, *38*, 467–476.

[11] Huang, Q.; Paull, B.; Haddad, P.R. *J. Chromatogr.* **1997**, *A770*, 3–11.

[12] Alimarin, I.P.; Ivanov, V.M.; Bol'shova, T.A.; Basova, E.M. *Fresenius' J. Anal. Chem.* **1989**, *335*, 63–69.

[13] Alimarin, I.P.; Basova, E.M.; Bol'shova, T.A.; Ivanov, V.M. *Zh. Anal. Khim.* **1986**, *41*, 5–34.

[14] Havel, J.; Khramov, A.N. *Scr. Fac. Sci. Nat Univ. Mas. Brun. (Chemia)* **1997–98**, 27–28, 51–62.

[15] Basova, E.M.; Bol'shova, T.A.; Shpigun, O.A.; Ivanov, V.M. *Zh. Anal. Khim* **1993**, *48*, 1094–1115.

[16] Doležal, J.; Sommer, L. *Coll. Czech. Chem. Commun.* **1997**, *62*, 1029–1042.

[17] Doležal, J.; Štepán, M.; Sommer, L. *International Congress on Analytical Chemistry*, Moscow, Russia, June 15–21, **1997**, Book of Abstracts, Abstract E-29.

[18] Vlašánková, R.; Otruba, V.; Bendl, J.; Fišera, M.; Kanický, V. *Talanta* **1999**, *48*, 839–846.

[19] Bidlingmeyer, B.A. *J. Chromatogr. Sci.* **1980**, *18*, 525–530.

[20] Hayakawa, K.; Nishijima, M.; Miyazaki, M. *Bunseki Kagaku* **1982**, *31*, 160–161. *Anal. Abstr.* **1982**, *43*, 4B186.

[21] Hayakawa, K.; Takizawa, T.; Furuta, M.; Miyazaki, M. *Bunseki Kagaku* **1983**, *32*, E243-E250. *Anal. Abstr.* **1984**, *46*, 4B181.

[22] Haddad, P.R.; Rochester, N.E. *Anal. Chem.* **1986**, *60*, 536–540.

[23] Hilton, D.F.; Haddad, P.R. *J. Chromatogr.* **1986**, *361*, 141–150.

[24] Rochester, N.E.; Haddad, P.R. *Chem. Austr.* **1987**, *54*, 164.

[25] Khramov, A.N.; Havel, J. *Scr. Fac. Sci. Nat. Univ. Mas. Brun. (Chemia)* **1997–98**, 27–28, 63–73.

[26] Mojski, M.; Gluch, I.; Obarski, N. *Chem. Anal. (Warsaw)* **1997**, *42*, 825–835.

[27] Steinbrech, B.; Schneeweiss, G.; Koenig, K.H. *Fresenius' J. Anal. Chem.* **1982**, *311*, 499–502.

[28] Nachtigall, D.; Artelt, S.; Wuensch, G. *J. Chromatogr. A* **1997**, *775*, 197–210.

[29] Vláčil, F.; Vinš, I.; Malícek, O. *Coll. Czech. Chem. Commun.* **1983**, *48*, 2255–2262.

[30] Timerbaev, A.R.; Tsoi, I.G.; Petrukhin, O.M. *J. Chromatogr.* **1990**, *498*, 337–348.

[31] Bol'shova, T.A.; Nesterenko, P.N.; Basova, E.M.; Morozova, N.B.; Ivanov, V.M. *Zh. Anal. Khim.* **1987**, *42*, 1648–1654.

[32] Doležal, J.; Sommer, L. *Coll. Czech. Chem. Commun.* **1994**, *59*, 2209–2226.

[33] Ohtsuka, C.; Matsukawa, K.; Wada, H.; Nagakawa, G. *Anal. Chim. Acta* **1992**, *256*, 91–96.

[34] Sommer, L.; Doležal, J. *Scr. Fac. Sci. Nat. Univ. Mas. Brun. (Chemia)* **1996**, *26*, 65–92.

[35] Voštová, J.; Sommer, L. *Coll. Czech. Chem. Commun.* **1976**, *41*, 1137–1168.

[36] Yotsuyanagi, T.; Hoshino, H.; Aomura, K. *Anal. Chim. Acta* **1974**, *71*, 349–354.

[37] Ivanov, V.M.; Gorbunova, G.N. *Zh. Anal. Khim.* **1980**, *35*, 2363–2368.

[38] Gorbunova, G.N.; Ivanov, V.M. *Zh. Anal. Khim.* **1980**, *35*, 705–712.

[39] Gorbunova, G.N.; Ivanov, V.M. *Zh. Anal. Khim.* **1982**, *37*, 880–886.

[40] Basova, E.M.; Bol'shova, T.A.; Ivanov, V.M.; Morozova, N.B. *Zh. Anal. Khim.* **1989**, *44*, 680–688.

[41] Nikitin, Yu.S.; Morozova, N.B.; Lanin, S.N.; Bol'shova, T.A.; Ivanov, V.M.; Basova, E.M. *Talanta* **1987**, *34*, 223–226.

[42] Basova, E.M.; Ivanov, V.M.; Morozova, N.B. *Zh. Anal. Khim.* **1990**, *45*, 671–678.

[43] Alimarin, I.P.; Nikitin, Yu.S.; Ivanov, V.M.; Bolśkava, T.A.; Basova, E.M. *Dokl. Akad. Nauk* **1986**, *288*, 1112–1115.

[44] Bol'shova, T.A.; Nesterenko, P.N.; Basova, E.M.; Ivanov, V.M. *Zh. Anal. Khim.* **1987**, *42*, 1648–1654.

[45] Uehara, N.; Annoh, Y.; Shimono, T.; Shijo, Y. *Anal. Sci.* **1989**, *5*, 111–112.

[46] Mueller, B.J.; Lovett, R.J. *Anal. Chem.* **1987**, *59*, 1405–1409.

[47] Mueller, B.J.; Lovett, R.J. *Anal. Chem.* **1985**, *57*, 2693–2699.

[48] Alimarin, I.P.; Basova, E.M.; Mishenina, T.V.; Bol'shova, T.A.; Shpigun, O.A. *Talanta* **1990**, *37*, 485–489.

[49] Wenclawiak, B.; Bickmann, F. *Bunseki Kagaku* **1984**, *33*, E67-E72 (1984). *Anal. Abstr.* **1984**, *46*, 10B163.

[50] Basova, E.M.; Bondareva, L.G.; Ivanov, V.M. *Zh. Anal. Khim.* **1992**, *47*, 1712–1719.

[51] Basova, E.M.; Ivanov, V.M; Bondareva, L.G.; *Zh. Anal. Khim.* **1996**, *51*, 954–960.

[52] Basova, E.M.; Bondareva, L.G.; Ivanov, V.M. *Zh. Anal. Khim. (Moscow)* **1997**, *52*, 36–42.

[53] Marsh, K.C.; Sternson, L.A.; Repta, A.J. *Anal. Chem.* **1984**, *56*, 491–497.

[54] Gurira, N.; Carr, P.W. *J. Chromatogr. Sci.* **1982**, *20*, 461–465.

[55] Li, L.; Li, D. *Sepn.* **1990**, *8*, 177–179. *Anal. Abstr.* **1991**, *53*, 7D76.

[56] Steinbrech, B.; Koenig, K.H. *Fresenius' J. Anal. Chem.* **1983**, *316*, 685–688.

[57] Koenig, K.H.; Ehmcke, H.V.; Schneeweiss, G.; Steinbrech, B. *Fresenius' J. Anal. Chem.* **1979**, *297*, 411–413.

[58] Khuhawar, M.Y.; Soomro, A. *Anal Chim. Acta* **1992**, *268*, 49–53.

[59] Prudnikov, G.K.; Garifzyanov, A.R.; Savel'eva, A.N.; Al-Hatib, D. *Zh. Anal. Khim.* **1992**, *47*, 1999–2003.

[60] Caroli, S.; Alimonti, A.; Petrucci, F.; La Torre, F.; Dominici, C.; Castello, M.A. *Ann. Inst. Super. Sanita* **1989**, *25*, 487–498.

[61] Cairns, W.R.L.; Ebdon, L.; Hill, C.J. *Anal. Proc.* **1994**, *31*, 295–297.

[62] Kizu, R.; Kaneda, M.; Miyazaki, M. *Anal. Sci.* **1992**, *8*, 145–150.

[63] Krull, I.S.; Ding, X.D.; Braverman, S.; Selavka, C.; Hochberg, F.; Sternson, L.A. J. *Chromatogr. Sci.* **1983**, *21*, 166–173.

[64] Abrams, M.J.; Murrer, B.A. *Science* **1993**, *261*, 725–730.

[65] Kelland, L.R.; Clarke, S.J.; McKlage, M.J. *Platinum Met. Rev.* **1992**, *36*, 178.

[66] Nuttal, K.L.; Gordon, W.H.; Oven, K.A. *Clin. Chem.* **1994**, *40*, 1787.

[67] Riley, Ch.M.; Sternson, L.A.; Repta, A.J.; Slyter, S.A. *Anal. Biochem.* **1983**, *130*, 203–214.

[68] Macka, M.; Borák, J.; Kiss, F. *J. Chromatogr.* **1991**, *586*, 291–295.

[69] Parsons, P.J.; Morisson, P.F.; LeRoy, A.F. *J. Chromatogr.* **1987**, *385*, 323–335.

[70] de Waal, W.A.J.; Maessen, F.J.M.; Kraak, J.C. *J. Chromatogr.* **1987**, *407*, 253–272.

[71] Ivanov, A.V.; Zheligovskaya, N.N.; Nesterenko, P.N. *Zh. Anal. Khim.* **1995**, *50*, 190–195.

[72] Burdakov, V.I.; Miteva, I.M. *Dokl. Bolg. Akad. Nauk* **1986**, *39*, 61–64.

[73] Macka, M.; Borák, J. *J. Chromatogr.* **1993**, *641*, 101–113.

[74] Branšteterová, E.; Kiss, F.; Miertuš, S.; Garaj, J. *Mikrochim. Acta* **1990**, *III*, 11–19.

[75] Ivanov, A.V.; Kitiashvili, K.D.; Ivanov, V.M. Vest. Moskovsk. Univ., Ser.2, *Khimia No2*, **1998**, *39*, 109–111.

[76] Dominici, C.; Alimonti, A.; Caroli, S.; Petrucci, F.; Castello, M.A. *Clin. Chim. Acta* **1986**, *158*, 207–215.

[77] Riley, G.M.; Sternson, L.A.; Repta, A.J.; Siegler, R.W. *J. Chromatogr.* **1982**, *229*, 373–386.

[78] Hansen, S.H. *J. Chromatogr.* **1989**, *491*, 175–185.

[79] Baldew, G.S.; Volkers, K.J.; deGoeij, J.J.M.; Vermeulen, N.P.E. *J. Chromatogr.* **1989**, *491*, 163–174.

[80] Baraj, B.; Sastre, A.; Martinez, M.; Spahiu, K. *Anal. Chim. Acta* **1996**, *319*, 191–197.

[81] Zhang, W.H.; Li, J.; Hu, Z.D. *J. Chromatogr. A* **1995**, *707*, 242–246.

[82] Pirogov, A.V.; Havel, J. *J. Chromatogr. A* **1997**, *772*, 347–355.

[83] Thornton, M.J.; Fritz, J.S. *J. Chromatogr. A* **1997**, *770*, 301–310.

[84] Hamáček, J.; Havel, J. *J. Chromatogr. A* **1999**, *834*, 321–327.

[85] Buchberger, W.; Semenova, O.P.; Timerbaev, A.R. *J. High. Resol. Chromatogr.* **1993**, *6*, 153–156.

[86] Buchberger, W.; Haddad, P.R. *J. Chromatogr. A* **1994**, *687*, 343–349.

[87] Kubáň, P.; Buchberger, W.; Haddad, P.R. *J. Chromatogr. A* **1997**, *770*, 329–336.

[88] Aquilar, M.; Farran, A.; Marti, V. *J. Chromatogr. A* **1997**, *778*, 397–402.

[89] Michalke, B.; Lustig, S.; Schramel, P. *Electrophoresis* **1997**, *18*, 196–201.

[90] Michalke, B.; Schramel, P. *Fresenius' J. Anal. Chem.***1997**, *357*, 594–599.

[91] Lustig, S.; Michalke, B.; Beck, W.; Schramel, P. *Fresenius' J. Anal. Chem.* **1998**, *360*, 18–25.

[92] Wenclawiak, B.W.; Wollman, M. *J. Chromatogr. A* **1996**, *724*, 317–326.

[93] Watanabe, E.; Nakajima, H.; Bina, E.; Hoshino, H.; Yotsuyanagi, T. *Bunseki Kagaku* **1983**, *32*, 469–474. *Anal. Abstr.* **1984**, *46*, 4B190.

[94] Zhang, H.S.; Mon, W.Y.; Cheng, J.K. *Talanta* **1994**, *41*, 1459–1463.
[95] Beketova, N.A.; Basova, E.M.; Ivanov, V.M.; Bol'shova, T.A. *Zh. Anal. Khim.* **1990**, *45*, 2178–2185.
[96] Basova, E.M.; Bol'shova, T.A.; Shpigun, O.A. *Zh. Anal. Khim.* **1993**, *48*, 284–296.
[97] Basova, E.M.; Bol'shova, T.A.; Shpigun, O.A. *Zh. Anal. Khim.* **1991**, *46*, 2362–2369.
[98] Basova, E.M.; Bol'shova, T.A.; Shapovalova, E.N.; Ivanov, V.M. *Zh. Anal. Khim.* **1990**, *45*, 1947–1954.
[99] Liu, Q.; Zhang, H.; Cheng, J. *Talanta* **1991**, *38*, 669–672.
[100] Shapovalova, E.N.; Mishenina, I.V.; Basova, E.M.; Bol'shova, T.A.; Shpigun, O.A. *Zh. Anal. Khim.* **1991**, *46*, 1503–1511.
[101] Liu, Q.P.; Zhao, T.; Liu, J.C.; Cheng, J.K. *Mikrochim. Acta* **1996**, *122*, 27–33.
[102] Liu, W.P.; Liu, Q.P. *Fresenius' J. Anal. Chem.* **1994**, *350*, 671–673.
[103] Liu, Q.P.; Wang, Y.C.; Liu, L.C.; Cheng, J.K. *Anal. Sci* **1993**, *9*, 523–528.
[104] Liu, Q.; Liu, J.; Tonk, Y.; Cheng, J. *Anal. Chim. Acta* **1992**, *269*, 223–228.

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Preconcentration of platinum group metals on modified silicagel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates

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Abstract

Modified silicagel (C18) was studied for separation and preconcentration of platinum group metals (Ru, Rh, Pd, Os, Ir and Pt) as ion associates of their chlorocomplexes with cation of onium salt N(1–carbaethoxypentadecyl)-trimethyl ammonium bromide. Sample containing HCl and the onium salt was pumped through the column. After elution with ethanol the eluate was evaporated in the presence of HCl. Resulting aqueous solutions were analysed with inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). Recovery values of 1–20 μg Pt and Pd from 50 ml of synthetic pure solution were 100 ± 3 and 100 ± 1%, respectively, however, they diminished with increasing sample volume and in the presence of the real sample matrix or nitrate ions. Samples of engine soot (NIES No. 8), decomposed by low pressure oxygen high-frequency plasma, and airborne particulates from dust filters of meteorological stations, leached with HNO_3 and H_2O_2, were analysed. A reasonable agreement was found between ICP-MS and ICP-AES results for airborne dust samples and the values comparable with those in literature were determined in NIES No. 8. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Platinum group metals; Ion associates; Inductively coupled plasma; Airborne particulates

1. Introduction

The determination of trace concentrations of platinum and palladium in environmental and biological samples has gained a considerable importance because of their toxicity and increasing occurrence, which is mainly due to industrial and automobile catalysts. Fresh air before the introduction of automobile catalysts contained 0.05 pg Pt m^{-3} and concentrations between 0.6 and 1.8 pg Pt m^{-3} were recently found in rural areas

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while in the neighbourhood of highways in Germany values between 1–13 pg Pt m^{-3} were determined in the ambient air [1]. Airborne dust collected at the area of Dortmund (FRG) during nearly a one-year period contained between 0.6 and 130 ng Pt g^{-1}, which corresponded to the concentration from 0.02 to 5.1 pg Pt m^{-3} in the air [2]. Pt-based catalytic converters cause the increase of concentration of platinum group metals (PGM) in soils next to highways and in the street or tunnel dust [3].

For the determination of these ultratrace concentrations the inductively coupled plasma mass spectrometry (ICP-MS) is sufficiently sensitive. The study of contamination of ambient air was performed using the ICP-MS instrumentation with electrothermal vaporisation (ETV-ICP-MS) which was applied to the analysis of particulates in automotive catalyst exhaust fractionated by inertial separation using a cascade impactor [4]. Detection limits were 0.2 pg of Ir, 0.3 pg of Pt, 0.4 pg of Rh, 0.7 pg of Pd, and laboratory measurements of catalysed car exhaust gave concentrations:150 ng Pt m^{-3}, 26 ng Rh m^{-3}, 2.5 ng Pd m^{-3}, 0.12 ng Ir m^{-3}, while field measurements in the highway tunnel yielded: 35 pg Pt m^{-3}, 285 pg Rh m^{-3}, 16 pg Pd m^{-3} and less than the detection limit for Ir [4]. For the determination of PGM in geological materials and also in the certified reference material NIES No. 8 (Vehicle Exhaust Particulates, Japan) these metals were preconcentrated using fire assay fusion and the collection into a NiS button prior to analysis with ETAAS [5]. Due to toxic properties of platinum, uptake of its compounds by plants and speciation to elucidate the metabolism of Pt in grass cultures were studied with size-exclusion chromatography coupled to ICP-MS [6].

Recently, modified silicagel Separon SGX C18 (particle size 7 mm) was found to be suitable for the preconcentration of 2–20 μg of Pt from 0.1 M HCl in the presence of cationic surfactants, especially dimethyllaurylbenzyl ammonium bromide, with subsequent elution with 96% ethanol. The recovery was 86–110% for 2 μg of Pt. The final emission spectrometry of Pt in plant ash matrix was carried out in 15 A dc-arc [7]. The preconcentration of ionic pairs is efficient also for some other elements, e.g. thallium (0.02–20 μg) which was successfully preconcentrated on silicagel C18 from 0.1 M HCl in the presence of various cationic surfactants as ion pairs with tetrachlorothallate(III) and subsequently eluted with 96% ethanol. Atomic emission spectrometry in a nitrous oxide-acetylene flame is suitable for the analysis of plants [8].

In this paper the simple selective preconcentration of Pt and Pd in the form of ion pairs of platinum(IV) and palladium(II) chlorocomplexes with cationic surfactant Septonex® on Separon™ SGX C18 column is used in combination with ICP-AES and ICP-MS for the determination of these elements in airborne particulates and the engine soot NIES No. 8. Besides Pt and Pd, the sorption of Au, Ru, Rh, Os and Ir was studied.

2. Experimental

2.1. Instruments

For analyses of environmental samples the ICP-MS instrument UltraMass (Varian, Australia) was used, which is installed at the laboratory of the ANALYTIKA Co. Ltd., Prague. Parameters of this instrument and operating conditions are presented below.

The ICP source was a generator with frequency 40.68 MHz operated at a power input of 1.2 kW and a reflected power of 7 W. A quartz plasma torch was provided with a corundum injector. Gas flows (Ar) were adjusted to the following values: plasma 14.5 l min^{-1}, auxiliary 1.2 l min^{-1}, carrier 0.94 l min^{-1}. A sampling depth was 6.5 mm. The V-groove nebulizer was fed by a peristaltic pump (1.5 ml min^{-1}). Internal standard (0.1 μg ml^{-1} of In) was on-line added to sample (1:2). Fast flush time was 10 s and stabilisation time when aspirating a sample was 15 s.

The mass spectrometer was a quadrupole mass filter. Ion optics voltages were optimised to the following values: extraction lens −416 V, 1st lens −234 V, 2nd lens −13.2 V, 3rd lens 0 V, 4th lens −72 V, photon stop −18 V, both entrance and exit plates 0 V. Measurement mode was peak-hopping with three points per peak and the separation of points was $\Delta m = 0.025$ AMU. Intensity was integrated within 100 scans and three blocks of scans were measured. The dwell time was 20 ms for m/z from 3 to 114, 5 ms for m/z from 115 to 188, 20 ms for m/z from 189 to 256. Isotopes: 197 Au, 101 Ru, 103 Rh, 105 Pd, 106 Pd, 108 Pd, 110 Pd, 189 Os, 193 Ir, 194 Pt, 195 Pt, 196 Pt; 115 In.

The ICP-AES instrument IRIS-AP (Thermo Jarrel-Ash, USA) at the laboratory of the Faculty of Chemistry of the Technical University Brno was used for measurements to optimise the sorption and for comparative measurements of selected real samples. Parameters of this instrument and operating conditions are presented below.

The ICP source was a generator with frequency 27.12 MHz operated at a power input of 1.15 kW. Gas flows (Ar) were: plasma 12 l min^{-1}, auxiliary 0.5 l min^{-1} and carrier 1.0 l min^{-1}. The Meinhard nebulizer was fed by a peristaltic pump (1.9 ml min^{-1}).

The spectral apparatus was an echelle-based spectrometer with a prism predisperser. The observation mode was the axial view. The detector was a CID type, integration time was 30 s and each result was the average of three measurements. The spectral lines (nm) in high spectral orders (values in parentheses) were used: Au I 242.795 (107); Ru II 240.272 (108); Rh II 233.477 (111); Pd I 340.458 (76); Os II 225.585 (115); Ir II 224.268 (116); Pt II 214.423 (121). Background-corrected intensities were evaluated for the analysis of samples.

A peristaltic pump ID-100 (Skala Brno, Medical Technology) was used for preconcentration.

A mineralisation device Plasma 1101 (IPC, CA), installed at the Department of Analytical Chemistry, Masaryk University Brno, produces high-frequency (13.5 MHz, 1500 W) low-pressure (10–500 Pa) oxygen plasma that facilitates the combustion of samples. The apparatus has six combustion chambers for parallel samples.

A microwave mineralisation device MDS 2000 (CEM, USA) installed at the laboratory of the ANALYTIKA Co. Ltd., Prague, is a closed system using vessels with PTFE inserts.

2.2. Chemicals

The multielement standard stock solution containing 100 mg ml^{-1} of Au, Ru, Rh, Pd, Os, Ir, Pt in 20% HCl (Astasol, ANALYTIKA, Prague, Czech Republic) was used for the preparation of working and calibration samples. The 0.1 M aqueous stock solution of the cationic surfactant Septonex, N(1-carbaethoxypentadecyl)-trimethylammonium bromide, $C_{21}H_{44}ONBr$ (Farmakon, Olomouc, CR) was used. For elution, ethanol 96% denaturated with 5% (v/v) methanol, was ultrasonically deaerated. Other chemicals used include: HNO_3, HCl, H_2O_2, NaCl, $NaNO_3$, $Mg(NO_3)_2.6H_2O$ (Lachema, Brno, CR) and surfactant BRIJ 35 (Merck, Darmstadt). All the chemicals were of analytical grade quality. SilicaCart^{TM} (Tessek, Prague) cartridges 9×20 mm with modified silicagel Separon^{TM} SGX, 60 μm were used for preconcentration.

2.3. Characteristics of samples

Airborne particulate matter was collected on glass filters at five meteorological stations of the Czech Hydrometeorological Institute in the Czech. Rep.: Kočkov, Všechlapy, Souš, Sokolov and Mědĕnec. The filters were exposed for 24 h with a flow rate of 720 m^3 day^{-1}.

The reference material NIES No. 8 (Vehicle Exhaust Particulates, National Institute for Environmental Studies, Japan) is certified only for Al, As, Ca, Cd, Co, Cr, Cu, K, Mg, Na, Ni, Pb, Sb, Sr, V, Zn. The only results of PGM in NIES No.8 were published after fire assay fusion and the collection into an NiS button followed by analysis with ETAAS [5].

3. Results and discussion

3.1. Sorption and elution procedures

The cartridge SilicaCart TM with sorbent was initially washed with 20 ml of 96% ethanol and 5 ml of 10–2 M aqueous solution of Septonex. Solutions containing PGM, Septonex and HCl were then pumped through the cartridge. For the desorption of ion associates of chlorocomplexes with quarternary base (Septonex), the 96% ethanol was pumped through the column and the first 4 ml of the eluate were collected to a calibrated test-tube containing 2 ml of 0.1 M HCl [7,8]. Owing to the known influence of volatile solvents on the ICP discharge stability the ethanol was evaporated in a Teflon® dish under an infrared lamp, the residue was transferred into a volumetric flask and filled up to the mark with 0.1 M HCl.

3.2. Selection of sorption conditions

To achieve maximum efficiency of the sorption, the concentrations of reagents were varied in these intervals: from 10^{-4} to 10^{-2} M of Septonex, from 0.02 to 0.3 M of HCl and from 0 to 0.5 M NaCl. Optimisation was performed with ICP-AES using the relaxation method.

Solutions for optimisation contained 20 μg of Au, Ru, Rh, Pd, Os Ir, and Pt in 50 ml, (0.1M HCl), i.e. their concentrations were 0.4 μg ml^{-1}. The behaviour of Au was studied as well, taking the advantage of its presence in the multielement standard solution. The sorption and desorption were performed as described in Section 3.1. The optimum concentration of Septonex was considered as the value at which maximum signals of all analytes in the solutions were achieved by desorption. This was found to be 0.006 M for Pt and Pd.

Test solutions containing 0.4 μg ml^{-1} of PGM and Au in 0.1 M HCl and 0.006 M Septonex were prepared for the evaluation of the sorption efficiency and the recovery of the preconcentration procedure. The set of calibration solutions containing 0, 0.1, 0.5, 1.0, 3.0 and 5.0 μg ml^{-1} of PGM and Au in 0.1 M HCl and 0.006 M Septonex was then prepared. The calibration lines with following values of coefficients of correlation, *r*, were obtained: Au 0.99989, Ru 0.99941, Rh 0.99964, Pd 0.99939, Os 0.99152, Ir 0.99988 and Pt 0.99987. Using these calibrations, the residual concentrations of PGM and Au were determined in the test solution outflowing at sorption procedure.

The efficiency of sorption was calculated based on a difference between the absolute amount of analyte brought onto the column in the test solution and the absolute amount of analyte determined in the test solution outflowing from the column, i.e. residual, not sorbed.

The recovery was determined based on the amount of analyte brought onto the column and the amount of analyte eluted with ethanol. It was found that the efficiency of sorption was practically the same as the recovery within the terms of experimental errors. In other words, the elution was considered quantitative.

The dependence of recovery on the concentration of Septonex is given in Fig. 1. The best recovery was achieved for Pd (100 ± 1)%, Pt (100 ± 3)%, and Au (100 ± 2)%. Slightly lower values were observed for Os (90 ± 9)% which reached recovery of 100% only at 0.01 M of Septonex, and for Ir (85 ± 5)%. Very poor sorption was observed for Ru (4%) and Rh (8%), thus, this system is not suitable for preconcentration of Ru and Rh. This may be due to the oxidation numbers of Ru and Rh and, consequently, due to the charge of corresponding complex anions, their distribution coefficients and formation of ion associates.

The influence of concentration of HCl on the recovery was not significant within the studied interval 0.02–0.3 M, as well as the influence of the concentration of NaCl in the range 0–0.5 M at the constant concentration 0.1M HCl.

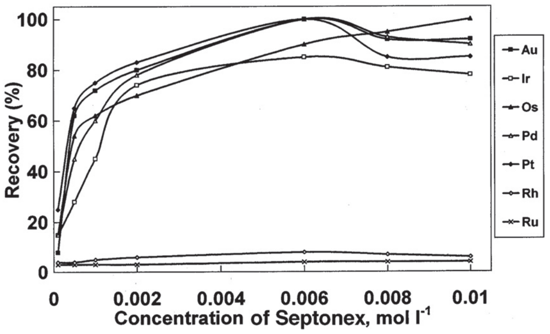

Fig. 1. Dependency of the efficiency of sorption of PGM on silicagel Separon™ SGX C18 on the concentration of Septonex. Conditions of sorption: 0.1 M HCl, 20 μg ml^{-1} of PGM and Au, sorption and elution flow rates: 0.6 and 1.5 ml min^{-1}, respectively.

Table 1
Recovery of PGM from pure solution, from leachate of airborne particulate matter and from model solutions spiked with hydrogen peroxide or sodium nitrate, and the relative standard deviation of repeatability for the pure solution

Analyte	Recovery of PGM (%)				RSD (%)[a]
	Pure solution[b]	Airborne dust[c]	H_2O_2 [d]	0.5 M NO_3^- [e]	Pure solution[b]
Au	100	82	90	74	2
Ru	5	7	1	5	13
Rh	10	0	2	2	26
Pd	100	22	100	54	1
Os	85	47	56	43	10
Ir	90	78	88	39	6
Pt	100	73	92	73	3

[a] Relative standard deviation of sorption obtained on 6 repetitions.
[b] Pure solution 50 ml) contained 0.4 mg ml^{-1} of PGM and Au, 0.006 M Septonex, 0.1 M HCl.
[c] Matrix of airborne dust leachate obtained from the procedure in Section 3.4.1
[d] 2 ml of H_2O_2 in 50 ml of solution with 0.4 mg ml^{-1} of each analyte, 0.006 M Septonex, 0.1 M HCl.
[e] 0.5 M $NaNO_3$ in 50 ml of solution with 0.4 mg ml^{-1} of each analyte, 0.006 M Septonex, 0.1 M HCl.

The recovery of PGM did not depend on the flow rate of sorption from 0.3 to at least 1.5 ml min^{-1}. Values > 1.5 ml min^{-1} were not studied due to the lack of suitable peristaltic tubings and pump speeds. Desorption was performed with the flow rate of 1.5 ml min^{-1} and the first 2 ml of ethanolic eluate contained the whole desorbed amount of analytes.

For further experiments, the 0.006 M Septonex, 0.1 M HCl, 0.6 and 1.5 ml min^{-1} sorption and desorption flow rates, respectively, were employed.

The influence of the sample volume on the sorption was studied due to large volumes of solutions prepared from airborne particulate matter. With increasing volume of the sorbed solution the recovery decreased so that above 1000 ml it approached 65%. This might be caused by washing out of the sorbed ion associate by a large volume of solution. Therefore, the application of the standard addition method was necessary for quantitative determination.

The recovery did not exhibit the dependence on the concentration of PGM and Au in the range from 20 ng ml^{-1} to at least 400 ng ml^{-1} at a sorption from 50 ml volume.

3.3. Repeatability of preconcentration

Six parallel preconcentrations were performed under the above optimum conditions from 50 ml of solution containing 20 μg of PGM and Au. Ethanolic eluates (4 ml) were treated as described in Section 3.1 and the resulting analysed solution was filled up to 10 ml volume. Samples were measured using ICP-AES. Relative standard deviations of repeatability and recovery values for pure solution in Table 1 show that the highest recovery and the lowest relative standard deviation (% RSD) of repeatability yielded Pd, Pt and Au.

3.4. Determination of Pd, Pt and Au in samples of airborne particulate matter

3.4.1. Decomposition procedure

Each glass filter was leached in a microwave device with 20 ml of HNO_3 and 4 ml of H_2O_2. The blank solutions characterising the whole procedure were prepared in the same way using unexposed filters. The leachate was transferred into a 250 ml volumetric flask, filled up to the mark and a portion of 100 ml was used for the determination of selected trace and matrix elements while 150 ml of the solution was used for the determination of PGM. To obtain a sufficient sample amount for preconcentration, the total volume of 26 one-day samples (each 150 ml) was taken as one sample. The corresponding volume of the air sample was thus 18720 m^3 for each site. The matrix contained (average):3 mg kg^{-1} Na, 10 mg kg^{-1} K, 20 mg kg^{-1} Ca, 1 mg kg^{-1} Mg, 10 mg kg^{-1} Al, 2 mg kg^{-1} Fe, 10 mg kg^{-1} B, 3–15 mg kg^{-1} Zn.

3.4.2. Influence of sample matrix on sorption

One of the solutions of airborne particulate matter was spiked with 0.4 mg ml^{-1} of PGM and Au. Original concentrations of PGM were very low, e.g. 5.7 ng ml^{-1} of Pd, 2.6 ng ml^{-1} of Pt and 7.3 ng ml^{-1} of Au. After the addition of Septonex (0.006 M) and hydrochloric acid (0.1 M), a 50 ml volume of this spiked solution was sorbed on the Separon^{TM} SGX. Recovery values of the added PGM concentrations in Table 1 show a significant decrease in comparison to pure solution, especially in the case of palladium. To recognise the component responsible for the sorption suppression, two sets of model solutions containing either H_2O_2 (0–2 ml/50 ml) or NO_3^- (0–0.5 M) were prepared and their sorption (50 ml) examined. While the hydrogen peroxide caused the significant diminuition of the sorption recovery only in the case of osmium, the presence of NO_3^- influenced the sorption of all analytes (Table 1). The explanation probably may be in the competitive formation and/or sorption of ionic associates of Septonex with nitrate anions.

The airborne dust was primarily sampled for the determination of elements other than PGM. Hence, the use of HCl had to be avoided due to known polyatomic interferences in the ICP-MS and the samples were thus decomposed using HNO_3. When special sampling would be for PGM determination, one could avoid the concurrent sorption problems by evaporating the aqua regia after leaching, followed by dissolution of a residue in HCl.

3.4.3. Analysis of leachates of airborne particulate matter

To the volume of 2500–3000 ml of a sample the stock solution of Septonex and HCl were added to obtain the final concentrations of 0.006 M Septonex and 0.1 M HCl. After sorption, elution and evaporation of ethanol the solution was filled up to 25 ml in the volumetric flask with 0.1 M HCl. Hence, the preconcentration by two orders of magnitude was performed.

Samples were analysed using both ICP-MS and ICP-AES. Limits of detection of ICP-MS, defined as concentrations corresponding to threefold of the standard deviation of the signal of the synthetic calibration blank solution, were 0.09 ng ml^{-1} of Pd, 0.05 ng ml^{-1} of Pt and 0.1 ng ml^{-1} of Au, limits of detection of axial ICP-AES, defined in the same way, were ~ 5 ng ml^{-1} of Pd, Pt or Au.The synthetic calibration blank solution contained 0.006 M Septonex and 0.1 M HCl.

Blank values corresponding to dummy filters were 4 ng ml^{-1} for Pd, 0.5 ng ml^{-1} for Pt and 2 ng ml^{-1} for Au. The standard deviation of repeatibility of measurement of the dummy filter blank solution using ICP-MS was 0.24 ng ml^{-1} for Pd, 0.16 ng ml^{-1} for Pt and 0.2 ng ml^{-1} for Au. The enriched sample solutions exhibited concentrations in ranges: 6–35 ng ml^{-1} of Pd, 3–16 ng ml^{-1} of Pt and 7–20 ng ml^{-1} of Au (except for 590 ng ml^{-1} of Au in the site Sokolov).

The precision of measurement with ICP-MS was characterised with RSD between 7% and 3% within above concentration range for airborne dust samples. After the dummy filter blank values were subtracted from found concentration values, the RSD of the blank-corrected concentrations increased to 24–5%. Limits of quantitatively determinable concentrations (LQDC) defined for 10% RSD of the concentration in pre-concentrated sample solution were 10 ng ml^{-1} of Pd, 5 ng ml^{-1} of Pt and 8 ng ml^{-1} of Au when taking into consideration the dummy filter blank value subtraction. The LQDC values of ICP-AES were 20 ng ml^{-1} of Pd, Pt, Au.

Obtained concentration values were recalculated using volumes of filtered air to content per cubic meter (Table 2). In some cases, a reasonable agreement was found between ICP-AES and ICP-MS results obtained on the same solution. However, the ICP-AES results have only a limited information meaning owing to the lower detection power. The reliability of ICP-MS results was supported with close values obtained on 2 isotopes of both Pt and Pd. Surprisingly high values of palladium and gold were found in the region of Sokolov, however, this city is in the centre of an

Table 2
Determination of Pt, Pd and Au in airborne dust by ICP-MS and ICP-AES (pg m^{-3})

Sampling station	Analyte					
	Pt		Pd		Au	
	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS
Kočkov	21	25^a; 36^b	nd	81^c; 27^d	nd	13
Všechlapy	62	19^a; 27^b	30	42^c; 45^d	13	16
Souš	16	15^a; 21^b	nd	nd^c; 23^d	nd	15
Sokolov	43	42^a; 41^b	280	253^c; 283^d	1410	1620
Měděnec	9	13^a; 24^b	31	67^c; 78^d	19	11

nd, not detected.
Isotopes, ^{a}195 Pt; ^{b}196 Pt; ^{c}105 Pd; ^{d}108 Pd.

industrial area (brown coal mines, thermal power plant). Nevertheless, all the other sites also exhibit concentrations of Pt and Pd that are two or three times higher in comparison to values reported for highway areas with heavy traffic [1–4]. This would be further examined.

3.5. Determination of platinum group metals in reference material NIES No. 8

3.5.1. Decomposition procedure

Reference material NIES No. 8 (0.5 g) was placed on the glass dish, wetted with BRIJ 35 and then several drops of the solution of $Mg(NO_3)_2$ were added to obtain a bulk residue after combustion [9]. The dish was dried under an infrared lamp and inserted into the combustion chamber of the PLASMA 1101 mineralisation apparatus. After the combustion (4 h) the ash was leached for 1.5 h with aqua regia (2 ml) at 60°C, the solution was diluted with distilled water (10 ml) and filtered through a sintered glass crucible, the filtrate was transferred into a 50 ml volumetric flask, the stock solution of Septonex was added to obtain its final concentration of 0.006 M and the sample filled up to the mark. This solution was then pumped through the SilicaCart™ with Separon™ SGX and the elution followed as described earlier. The sample was transferred to a 25 ml volumetric flask because of the need to preserve some solution for possible comparison measurement, however, the final volume can be reduced to 5–2 ml which could result in a preconcentration factor of 10–25.

3.5.2. Analysis of engine soot

Six parallel samples were prepared by procedure described in the Section 3.5.1 and they were analysed using ICP-MS. Results presented in Table 3 show large differences between individual determinations. One of the reasons may be the inhomogeneity of this standard reference material in respect to the PGM, already reported in Ref. [5]. This inhomogeneity may be due to the metallic character of PGM particulates and, hence, different distribution in the engine soot in comparison to other elements. However, excluding the extreme result for Pt in the sample no. 2 we obtain an average value of 160 ng g^{-1} of Pt with the standard deviation of 90 ng g^{-1} of Pt which is close to 185 ng g^{-1} of Pt found by Paukert and Rubeška [5] (Table 3). Similarly, six parallel determinations yielded 230 ng g^{-1} of Pd (the standard deviation is 94 ng g^{-1} of Pd), which is compara-

Table 3
Determination of Pt, Pd, Ir and Au in reference material NIES No. 8 vehicle exhaust particulates ng g^{-1})

Sample no.	Analyte			
	Pt	Pd	Ir	Au
1	66	189	5	182
2	1259	332	35	601
3	193	365	87	163
4	90	147	5	38
5	296	158	20	111
6	155	188	3	94
x^a_{ref}	185 ± 14	180 ± 28	39 ± 21.1	—

^{a} average value ± standard deviation, taken from Ref. [5].

ble with 180 ng g^{-1} of Pd reported in [5] (Table 3). The larger standard deviations of our results in comparison with those obtained by Paukert and Rubeška [5] (Table 3), may be influenced also by the amount of sample taken for decomposition (2 g reported in [5]). However, there is a reasonable agreement between our results and ETAAS values after preconcentration to NiS button [5].

4. Conclusion

Preconcentration technique based on the sorption of ion associates of chlorocomplexes of platinum group metals with the surfactant N1-carbaethoxypentadecyl)-trimethylammonium bromide on the modified silicagel C18 was developed and applied to the determination of the platinum group metals in airborne dust collected on the air filters, and in certified reference material NIES no. 8 Vehicle Exhaust Particulates). Inductively coupled plasma mass spectrometry was suitable for the analysis of enriched samples. Concentrations of Pt and Pd on the level of tens of pg m^{-3} were found in air filtered through the filters installed in six Czech meteorological stations. Reasonable agreement was found with results obtained on NIES no. 8 by ETAAS values after preconcentration to NiS button [5].

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References

[1] Platinum, Environmental Health Criteria 125, World Health Organization, Geneva, 1991.

[2] F. Alt, A. Bambauer, K. Hoppstock, B. Mergler, G. Tölg, Fresenius J. Anal. Chem. 346 (1993) 693.

[3] M. Parent, H. Vanhoe, L. Moens, R. Dams, Fresenius J. Anal. Chem. 354 (1996) 664.

[4] C. Luedke, E. Hoffmann, European Winter Conference on Plasma Spectrochemistry, 12–17 January 1997, University of Gent, Gent, Belgium, 1997.

[5] T. Paukert, I. Rubeska, Anal. Chim. Acta 278 (1993) 125.

[6] D. Klueppel, N. Jakubowski, J. Messerschmidt, D. Stuewer, D. Klockow, European Winter Conference on Plasma Spectrochemistry, 12–17 January 1997, University of Gent, Gent, Belgium, 1997.

[7] V. Otruba, M. Strnadová, B. Skalníková, Talanta 40 (1993) 221.

[8] V. Otruba, J. Stepánková, L. Sommer, Talanta 41 (1994) 1185.

[9] V. Otruba, J. Kaláček, Chem. Listy 87 (1993) 64.

Příloha 4

KOMENDOVA-VLASANKOVA, R. a SOMMER L.
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SEPARATION AND PRECONCENTRATION OF PLATINUM GROUP METALS AND GOLD ON MODIFIED SILICA AND XAD SORBENTS IN THE PRESENCE OF CATIONIC SURFACTANTS FOR THEIR DETERMINATION BY ICP-AES

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Various modified silica sorbents and unmodified silica were tested for the separation and preconcentration of 10–200 ng cm^{-3} from 50–1 000 cm^3 sample volume of platinum group metals (PGMs), Pt(IV, II), Pd(II), Ir(IV), Rh(III), Os(VI), Ru(IV) and Au(III) in the form of ion associates of their chloro and bromo complexes with cationic surfactants. [1-(Ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Septonex®), benzyl(dodecyl)dimethylammonium bromide (Sterinol®), trimethyl(tetradecyl)ammonium bromide or hexadecyl(trimethyl)ammonium chloride and 0.1 M HCl or 0.1 M HBr are suitable for the purpose. 100% recovery for Pd(II), Pt(IV) and Au(III) was obtained with octadecyl silicas Separon™ SGX C18, Separon™ SGX RPS and Phenyl™ silica in the presence of 0.006 M Septonex® or 0.003 M Sterinol®. The retained PGMs and Au(III) were eluted with acetonitrile and determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) after evaporation of organic solvent in the presence of 0.1 M HCl. The enrichment factor on Separon™ SGX RPS reaches 100. A 1 000 : 1 excess of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+} or Al^{3+} does not interfere with the preconcentration of PGMs and Au(III) on this sorbent. With the silica-based anion exchanger Separon™ SGX AX, the 100% recovery is observed for Ir(IV), Pd(II), Pt(IV) when the elution is performed with 5 M HCl or 5 M HNO_3. Macroporous sorbents Amberlite™ XAD2 and Amberlite™ XAD4 are suitable for the retention of Au(III), Pd(II) and Pt(IV) from 0.1 M HCl and 0.006 M Septonex®. 100% recovery is achieved using acetonitrile as eluent but there is no preference of these sorbents to modified silica. In this way, the recovery of 0.1–0.2 μg cm^{-3} Au(III), Pd(II), Pt(IV) was also successfully tested with spiked matrices of soil extracts, power station dust samples and natural waters.

Keywords: Platinum group metals; Gold; Sorbents; Modified silica; Amberlite XAD2 and XAD4; Quaternary ammonium surfactants; Inductively coupled plasma atomic emission spectrometry (ICP-AES).

Recently, the platinum group metals (PGMs) awoke a considerable interest because of their increased occurrence in the environment. This is due to

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their use as industrial and automobile catalysts and application of some platinum(II) complexes as anti-cancer drugs[1]. Thus, microamounts of PGMs are dispersed in the ambient air, airborne dust particles, road dust, soil and plants near the busy highways and waters[1–3]. The platinum content of the airborne dust ranged from 0.6 to 130 ng g^{-1}, in air from 0.02 to 5.10 pg m^{-3} and in motorway soils from 15 to 30 ng g^{-1} (ref.[4]). Platinum has to be monitored in body fluids and tissues in cancer treatment and Pt(II) traces may appear on the furniture in rooms or in waste-waters of some hospitals[5]. Several compounds of Pt(IV) and Pd(II) are gastrointestinal irritants and strong allergens already in the nanogram level for sensitive persons[1,2]. Gold contents in the environment are also low, *i.e.* 0.05 ng cm^{-3} of Au was found in sea-water and 0.09 and 0.2 ng cm^{-3} in river- and spring-water, respectively, but the average concentration in the Earth crust 4 ng g^{-1} was reported[6].

The widely used inductively coupled plasma atomic emission spectrometry (ICP-AES) can be successfully used for simultaneous determination of PGMs and Au in limit concentrations below μg cm^{-3} without preconcentration. Moreover, the accompanying common metals and a large excess of acids and inert salts may interfere[3,7–9].

Modified and unmodified silica coated with more and less strongly retained organic reagents have been already reported for separation of PGMs (ref.[10]). Octadecyl silica was already used for the preconcentration of Pt(IV) in the form of ion associate of hexachloroplatinate with various cationic surfactants, in particular benzyl(dodecyl)dimethylammonium bromide prior to its determination by emission spectrometry in spiked plant ash[11].

Recently, the retention of several PGMs and Au(III) in the form of ion associates of chloro complexes with [1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide was studied on octadecyl silica only. The recovery of preconcentrated metals was evaluated by ICP-AES and inductively coupled plasma mass spectrometry[12] (ICP-MS). At present, ICP-MS was only suitable for their direct determination in airborne dust particulates, usual soils, waters and plant tissues[8,13–15]. This approach was then used for testing analytical performance characteristics of various types of inductively coupled plasma spectrometers[16]. A selective preconcentration of gold was also described on octadecyl silica in the form of ion associates of Au(III) chloro complex and Au(I) cyano complex with quaternary bases including some cationic surfactants[17].

In this paper, a number of modified silicas, silica-based anion exchangers, Amberlite™ XAD2, XAD4 and LiChrolut™ EN polymers are tested and compared for simple selective separation, preconcentration and recovery of PGMs and Au(III) in the form of ion pairs of chloro and bromo complexes in the presence of various cationic surfactants. After elution, multicomponent determination follows by ICP-AES.

EXPERIMENTAL

ICP-AES Instrumentation and Operation Conditions

Final measurements were carried out on an echelle-based ICP spectrometer with a prism predisperser IRIS AP™ (Thermo Jarrell Ash, U.S.A.) containing a CID detector with 512 × 512 pixels for 195–900 nm and axial plasma discharge. The echelle grating contained 54.4 lines mm^{-1}, the plasma source was a generator with 27.12 MHz which operated with a power output of 1.15 kW. The plasma argon flow rate was 12 dm^3 min^{-1}, that of the auxiliary argon was 0.5 dm^3 min^{-1} and carrier 1.0 dm^3 min^{-1}. The signal integration time was 30 s and every result was the average of three measurements. The continuous background correction minimised the noise of the plasma and of solutions with high salt concentrations. The Meinhard nebulizer was fed by a peristaltic pump (flow rate 1.85 cm^3 min^{-1}).

The following spectral lines (nm) in high orders were used for evaluation (orders in parentheses): AuI 242.795 (107), RuII 240.272 (108), RhII 233.477 (111), PdI 340.458 (76), OsII 225.585 (115), IrII 224.268 (116), PtII 214.423 (121). Background-corrected intensities were evaluated for the analysis of samples.

Four-point calibration plots were made for different spectral lines of PGMs and Au in the concentration range 0–2 mg dm^{-3} with correlation coefficients of 0.9998–0.9999. Calibration solution was prepared in 0.1 M HCl and various amounts of surfactants being used, which influenced the plots.

The instrumental detection limits (*cf.* Table I) are based on the 3σ definition[18] and were evaluated from 10 measurements of the blank solutions containing 0.1 M HCl and 0.006 M cationic surfactant Septonex® or 0.003 M Sterinol®.

Sorbents

The following modified silica sorbents were used in plastic cartridges 20 × 9 mm with sorbent particles of 60 μm size (Tessek, Prague, Czech Republic): octadecyl silica (Separon™

TABLE I
Limits of detection (in μg cm^{-3}) on IRIS AP™ ICP spectrometer[a]

Surfactant	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
Septonex	0.0026	0.0073	0.0019	0.0066	0.0053	0.0062	0.0035
Sterinol	0.0034	0.0050	0.0038	0.0065	0.0043	0.0102	0.0041

[a] Average values for blank solutions containing 0.1 M HCl and 0.006 M Septonex® or 0.003 M Sterinol®.

SGX C18 and Separon™ SGX RPS), octyl silica (Separon™ SGX C8), cyanoethyl silica (Separon™ SGX CN), phenyl silica (Separon™ SGX Phenyl), aminopropyl silica (Separon™ SGX NH_2), silica (Separon™ SGX), a strong basic anion exchanger (Separon™ SGX AX).

Modified-silica-based sorbents LiChrolut™ RP-18, LiChrolut™ RP-18e (particle size 40–60 µm, Merck, Darmstadt), macroporous styrene–divinylbenzene polymers LiChrolut™ EN (particle size 40–120 µm), and Amberlite™ XAD2 and Amberlite™ XAD4 (particle size 0.3–0.9 mm, Merck Darmstadt, Germany) were ground and sieved to 63–100 µm particle size. The last two were filled into 2.5-cm^3 plastic columns of MoBiTec (Göttingen, Germany).

Chemicals and Solutions

A multielement standard stock solution contained 100 mg dm^{-3} of Pt(IV), Rh(III), Ir(IV), Os(IV), Ru(IV), Pd(II) and Au(III) as chloro complexes in 20% HCl (Astasol MIX, Analytica, Prague, Czech Republic). Bromo complexes of platinum metals or gold resulted when solutions of their chloro complexes containing 1 mg of PGMs and Au and 5% HCl were heated for 60 min with 10 ml of 46% HBr almost to the boil. The excess of HBr was removed by partial evaporation. After dilution with water to the final volume, the metal concentration was 8 mg dm^{-3} and the HBr concentration was 0.2 mol dm^{-3}. The transformation of PGM and Au(III) chloro complexes to bromo complexes is assumed to be complete although the presence of some anionic mixed chloro bromo complexes of Pt(IV) and P(II) is possible[19]. The transformation was followed by comparison of absorption spectra[20].

Reduction of PGM and Au(III) with hydrazine hydrate. The standard stock solution in 20% HCl was heated for 30 min with 0.80% hydrazine hydrate. After cooling, the solution was diluted with 4 м HCl to 25 cm^3. It contained 8 mg dm^{-3} of PGMs and Au. In this way, Pt(IV) was reduced to Pt(II), Au(III) to Au(I) and Au(0), and Ir(IV) to Ir(III).

Cationic surfactants. [1-(Ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Septonex®; Farmakon, Olomouc, Czech Republic), benzyl(dodecyl)dimethylammonium bromide (Sterinol®; Galenus, Warsaw, Poland), trimethyl(tetradecyl)ammonium bromide (Merck, Darmstadt, Germany), hexadecyl(trimethyl)ammonium chloride and 1-hexadecylpyridinium chloride hydrate (Fluka, Switzerland) were used in 0.1 м stock solutions.

Humic acid 244 MAR was a low-molecular-weight sample of the Research Institute of Inorganic Chemistry (Ústí nad Labem, Czech Republic), prepared from oxyhumolite originating from Bohemian brown coal. The stock solution contained 1 g of humic acid in 500 cm^3. The sample was previously dried over phosphorus pentoxide and finally transformed into the ammonium salt in an exsiccator over concentrated ammonia during 24 h.

All the other used chemicals and solvents were of analytical grade purity from Lachema Brno, Analytika, Ltd. Prague and Aldrich and Fluka companies.

Characteristics of Tested Samples

Three soil extracts in *aqua regia* were samples of the Central Institute for Supervising and Testing in Agriculture (Brno, Czech Republic) containing certified macro- and microelements (S, As, Mo, Zn, Pb, Co, Cd, Ni, V, Be, Cu, Cr, P, Mn, Fe, Mg, Ca, Al, K, Tl).

Power-station fly-ash was a reference material from the Czechoslovak Metrological Institute (Bratislava, Slovakia) certified for main components such as Al, Ca, K, Fe, Mg, Na, Si, Ti and traces of As, Ba, Ce, Co, Cr, Cs, Cu, Eu, La, Mn, Pb, Rb, Th, V, Zn.

Water samples were from a Moravian river (National Park Podyjí) and peat moor water (Velké Dářko).

PGMs and Au(III) were always absent in samples which was confirmed by ICP-MS (ref.[21]). Thus, they were spiked into the samples for testing their recovery in particular matrices by the procedures mentioned below.

Retention and Elution Arrangement

Solutions were simultaneously pumped through repeatedly used plastic cartridges with the sorbents placed in a water-pump-operated vacuum suction device DORCUS™ (Tessek, Prague, Czech Republic). A peristaltic pump UNIPAP 315™ (Poland) was attached with a 3-mm silicone tubing to the cartridges and operated with an optimised solution flow rate of 1 cm^3 min^{-1}. The recovery of PGMs and Au did not depend on the flow rate of sorption from 0.3 to at least 1.5 cm^3 min^{-1}. Higher values were not used[12] to guarantee the highest effectivity of retention.

Sorption and Elution Procedures on Modified Silica and Amberlite™ XAD2 and XAD4 Sorbents

A cartridge with the sorbent was first washed with 10 cm^3 of 96% ethanol and then conditioned with 10 cm^3 of surfactant solution with selected concentration. Optimisation studies were carried out with 50 cm^3 of a sample solution containing 20 µg of PGMs and Au(III) as chloro or bromo complexes, 0.1 M HCl and a surfactant at a selected concentration. 0.1 M HCl is an optimum since higher concentrations decrease the sorption efficiency by partial damage of the hydrophobic sorbent surface. Lower contents of the acid cause losses of PGMs and Au(III) on the surface of dishes. The metal species were eluted from the sorbents with 10 cm^3 of CH_3CN. An amount of 1 cm^3 of 0.1 M HCl was added to the eluate and the solution evaporated in a suitable Teflon™ dish to 1 cm^3, the residue was diluted to 10 cm^3 in a volumetric flask and analysed by ICP-AES. For sorbents Amberlite™ XAD2 and XAD4, new cartridges must be always used.

The cartridges with Separon™ SGX AX in the DORCUS™ arrangement were washed with 10 cm^3 of distilled water and the retention was studied from 50 cm^3 of a sample containing 20 µg PGMs and Au(III), 0.1 M HCl or 0.1 M HBr. Sodium perchlorate and mineral acids of various concentrations were used for elution.

The recovery was always calculated from the known amount of PGMs and Au(III) in the used dilute standard solution and the evaluated value in the eluate. The confidence interval of mean recovery resulted from 3 or 6 independent retentions and elutions. The span between the lowest and highest values of the variation interval of parallel experiments was used for the statistical evaluation of recovery[22].

RESULTS AND DISCUSSION

Effect of Solvents

A number of solvents were tested as eluents (*cf.* Table II) with a similar effect for Au(III), Pd(II), Pt(IV), Os(VI), Ir(IV) but acetonitrile is recommended because of 100% recovery for Au(III), Pt(IV) and Pd(II) and 80–90% recovery for Ir(IV) and Os(VI).

Effect of Surfactant

The effect of Septonex®, Sterinol®, trimethyl(tetradecyl)ammonium bromide, hexadecyl(trimethyl)ammonium chloride and 1-hexadecylpyridinium chloride was studied in the 0–0.01 M concentration interval after sorption and desorption of PGMs and Au(III) on Separon™ SGX C18. Similar plots were obtained for the other kinds of modified silica used. The kind of surfactant and its concentration in solution significantly influences the sorption of PGMs and Au(III). For 0.006 M Septonex® and 0.003 M Sterinol®, the recovery is nearly 100% from 0.1 M HCl for Au(III), Pd(II) and Pt(IV), 85–90% for Os(VI) and Ir(IV); however, the sorption of Rh(III) and Ru(IV) are far from being quantitative. The 0.006 M trimethyl(tetradecyl)ammonium chloride and hexadecyl(trimethyl)ammonium chloride are suitable for the recovery of Au(III) and Pd(II) but not suitable for Pt(IV). 1-Hexadecylpyridinium chloride should not be used for the sorption under above conditions since the ion associates of the chloro complexes of PGMs and Au(III) are strongly bonded to the sorbent. The elution efficiency is low for all PGMs when 10 cm^3 of acetonitrile, ethanol, methanol, propan-2-ol, acetone or even 0.5 M thiourea in acid solution were used as eluents.

TABLE II
Average recovery (in %) of PGMs and Au(III) after elution with various solvents from Separon™ SGX C18[a]

Eluent	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
Ethanol	100	88	90	100	101	6	25
Methanol	100	95	86	96	100	12	60
Propan-2-ol	100	87	68	101	97	12	60
Acetone	96	95	76	101	97	11	60
Acetonitrile	101	89	91	101	99	13	68

[a] PGMs and Au(III) (20 µg) were retained as chloro complexes from 50 cm^3 solution in the presence of 0.006 M Septonex® and 0.1 M HCl. Average recoveries were calculated from 3 independent experiments.

The formation of micelles in solutions with surfactant concentrations ≥ 0.008 mol dm^{-3} for all the used surfactants competes with the sorption of chloro complexes of PGMs and Au(III) (*cf*. Fig. 1). More than 0.01 M surfactant in solution also interferes by clogging the columns.

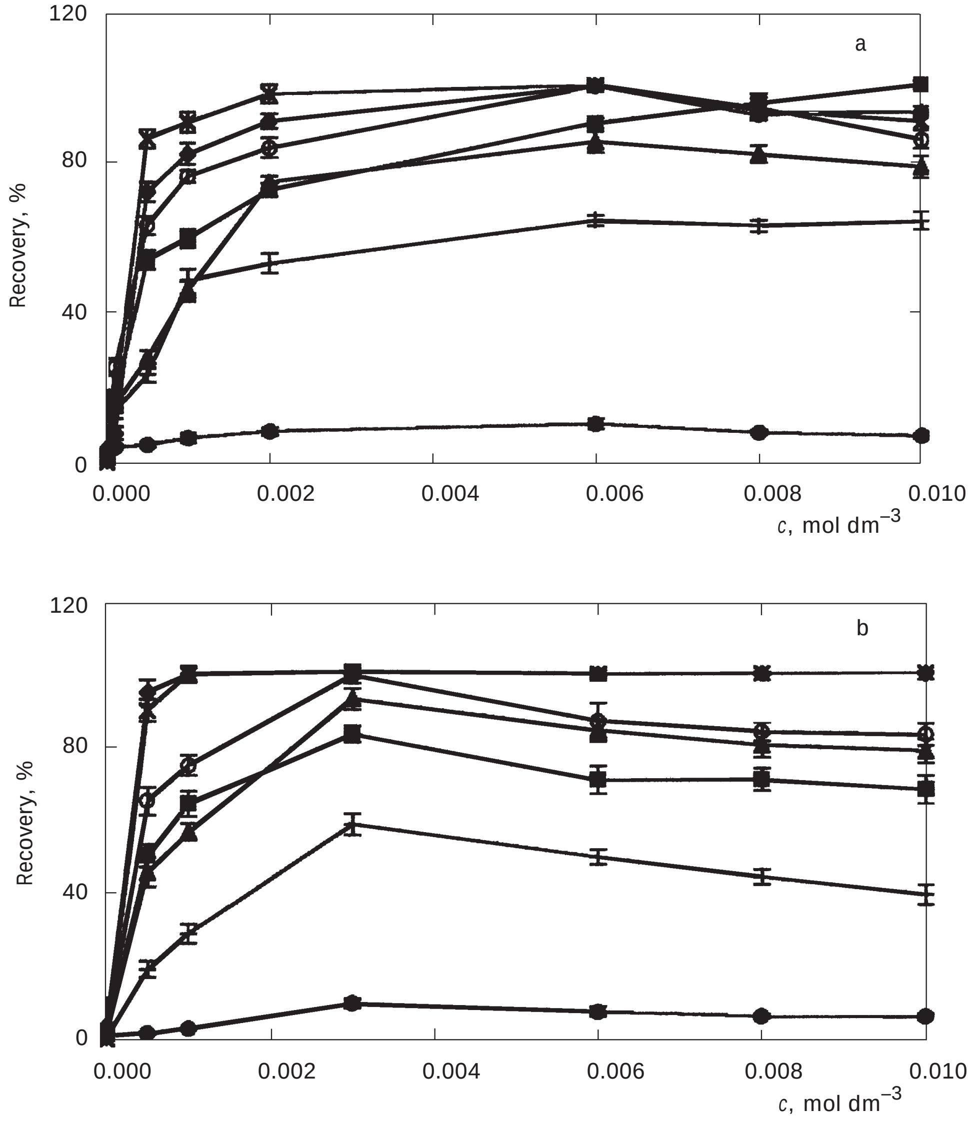

FIG. 1

Effect of concentration of Septonex® (a) and Sterinol® (b) on the recovery of PGMs and Au(III) on Separon™ SGX C18. An amount of 50 cm^3 from a sample solution containing 20 μg of PGMs and Au(III), 0.1 M HCl and surfactant of a selected concentration was applied onto Separon™ SGX C18; elution was carried out with 10 cm^3 of acetonitrile. The segments correspond with the confidence interval from 3 experimental values. ◆ Au, ■ Ir, ▲ Os, × Pd, ❍ Pt, ● Rh, + Ru

Effect of Various Modified Silica Gel Sorbents

100% recovery resulted for Au(III), Pd(II) and Pt(IV) on conditioned Separon™ SGX C18, Separon™ SGX RPS, Separon™ SGX C8, Separon™ SGX Phenyl and Separon™ SGX CN sorbents (*cf*. Fig. 2) when 50 cm^3 of sample solutions containing 20 µg of PGMs and Au(III), 0.1 M HCl and the optimum 0.006 M Septonex®, trimethyl(tetradecyl)ammonium bromide, hexadecyl(trimethyl)ammonium chloride or 0.003 M Sterinol® were used for the retention and 10 cm^3 of acetonitrile for elution. A low recovery was observed for Rh(III) and Ru(IV) for all the tested sorbents and surfactants. The phenyl silica Separon™ SGX Phenyl (*cf*. Table III) and Separon™ SGX C18 are most suitable for the sorption of Ir(IV) and Os(VI) in the presence of Sterinol® or Septonex®. Sorbents Separon™ SGX and SGX NH$_2$ are unsuitable since no retention of metal complexes resulted even when the column was conditioned by the surfactant. The behaviour of silica, Separon™ SGX, proves the necessity of hydrophobic surface of the sorbent but the processes on modified hydrophobic silica may be complex. The dynamic retention of the surfactant is assumed to proceed on the sorbent surface, as

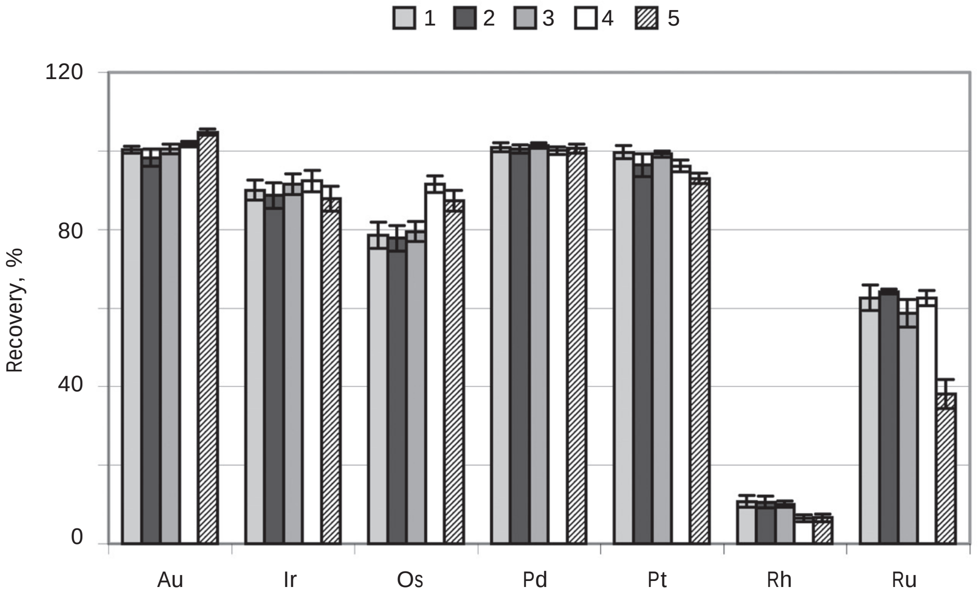

FIG. 2
Recovery of PGMs and Au(III) after sorption on various sorbents. An amount of 50 cm^3 from a sample solution containing 20 µg of chloro complexes of PGMs and Au(III), 0.006 M Septonex® and 0.1 M HCl was applied onto Separon™ SGX C18 (1), Separon™ SGX C8 (2), Separon™ SGX RPS (3), Separon™ SGX Phenyl (4) and Separon™ SGX CN (5). The segments correspond with the confidence interval from 3 experimental values

far as the sorbent surface has been previously saturated with the surfactant. The anionic PGMs and Au halo complexes are then retained on the sorbent surface. Such process, however, may be accompanied by the direct bonding of the ion associate on the column because the ion association between large anionic halo complexes and cationic agents is commonly assumed to occur in solution during extraction processes.

No retention of PGMs and Au(III) was observed in the absence of cationic surfactant in solution and without previous conditioning of the sorbents with the surfactant. In addition, no retention took place when non-ionic surfactant such as Triton X-100™ was used in concentrations of 0.01–0.006 mol dm^{-3}.

The low retention efficiency and recovery of Rh(III) and Ru(IV) is caused by a complex equilibrium in 0.1 M HCl containing partial aquation and hydrolysis of chloro complexes to monomeric and oligomeric species[19,23–25] without or with different charges whose tendency to form ion associates with cationic surfactants decreased. The incomplete retention of Ir(IV), Os(VI), Rh(III) and Ru(IV) was also proved by analysis of effluents from the column after sorption which contained the rest of the PGMs (*cf.* Table IV).

Separon™ SGX NH_2 gives a very low sorption efficiency for PGMs and Au(III) under all tested conditions even in the presence of surfactant on the

TABLE III
Average recovery (in %) of PGMs and Au(III) from Separon™ SGX Phenyl and Separon™ SGX RPS in the presence of various cationic surfactants[a]

Surfactant	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
6 mM Septonex[b]	98.9 ± 1.0	92.8 ± 1.2	82.3 ± 1.3	100.9 ± 0.8	98.4 ± 1.4	12.2 ± 1.1	58.8 ± 0.9
6 mM Septonex	100.7 ± 0.7	92.3 ± 1.4	91.5 ± 2.1	100.1 ± 0.9	96.2 ± 1.5	6.6 ± 0.9	62.5 ± 1.9
3 mM Sterinol[b]	98.5 ± 1.7	78.2 ± 1.8	79.6 ± 1.9	99.8 ± 0.9	97.9 ± 3.7	15.9 ± 1.3	56.8 ± 1.6
3 mM Sterinol	100.3 ± 0.4	98.3 ± 2.5	83.3 ± 1.4	100.3 ± 0.6	100.8 ± 0.6	17.0 ± 0.9	49.5 ± 1.8
6 mM TTAB	98.8 ± 2.4	53.0 ± 3.0	39.8 ± 2.1	100.3 ± 0.8	56.7 ± 3.1	17.3 ± 1.1	39.0 ± 2.6
6 mM CTAC	100.5 ± 1.9	49.4 ± 3.6	53.2 ± 3.8	100.3 ± 0.7	67.3 ± 1.3	4.2 ± 0.5	26.2 ± 2.3

[a] PGMs and Au(III) (20 μg) were retained as chloro complexes from 50 cm^3 solution in the presence of surfactant and 0.1 M HCl. Confidence intervals were calculated at the level of significance $\alpha = 0.05$ from 3 independent repetitions. [b] Separon™ SGX RPS, confidence intervals were calculated from 6 independent repetitions.

sorbent and in the solution. This is surprising since this sorbent should behave as weak anion exchanger.

After heating the sample with 0.8% hydrazine hydrate solution in 20% HCl, Pt(IV) is reduced to Pt(II) which is also retained. The recovery of 20 μg of PGMs with Separon™ SGX C18 from 50 cm^3 of a solution containing 0.1 M HCl and 0.006 M Septonex® remains nearly 100% for Pd(II), Pt(II) and Ir(III), that of Os(III) and Ru(III) increases in comparison with Os(VI) and Ru(IV) in solution without reductant but is not quantitative. The extremely low sorption efficiency of gold is due to Au(I) and Au(0) formed in reduction.

The sorption efficiency of analogous LiChrolut™ RP-18 and LiChrolut™ RP-18e is comparable with previous sorbents under analogous optimum conditions. Polymer LiChrolut™ EN, however, is not suitable for the retention because of its very low sorption efficiency for the metals (Fig. 3).

Effect of Sample Volume and PGMs and Au(III) Contents

The sorption efficiency for 10–200 ng cm^{-3} of Au(III), Pd(II) and Pt(IV) on silica Separon™ SGX RPS little depends on the sample volume between 50 and 1 000 cm^3 as well as on the common limit of determination by inductively coupled plasma atomic emission spectrometry, which corresponds to the enrichment factor up to 100. The solutions contain the standard stock solution of PGMs and Au(III), 3 cm^3 of 0.1 M Sterinol® or 6 cm^3 of 0.1 M Septonex® and 0.1 M HCl; acetonitrile was the eluent. For Ir(IV), Os(VI), Rh(III), Ru(IV), the sorption efficiency rapidly decreased with increasing sample volume (Table V).

TABLE IV
Retention of PGMs and Au(III) on Separon™ SGX C18[a]

Retention	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
Retained, %	100	93	83	101	100	10	61
Passed, %	0	7	17	0	0	90	39

[a] PGMs and Au(III) (20 μg) were retained as chloro complexes from 50 cm^3 solution in the presence of 0.006 M Septonex® and 0.1 M HCl. Average recoveries were calculated from 3 independent experiments.

Similarly, no effect of metal concentration on the sorption efficiency was observed for 10–200 ng cm^{-3} of Au(III), Pd(II) and Pt(IV) when sorbed from 100 cm^3 of a solution containing 0.006 M Septonex® or 0.003 M Sterinol® and 0.1 M HCl, but a considerable sorption efficiency decrease was again observed with Ru(IV), Os(VI), Ir(IV), Rh(III) from solutions containing less than 50 ng cm^{-3}. No washing-out effect was observed for the retained ion associate for ≥10 ng cm^{-3} Pt(IV), Pd(II) and Au(III) in 50–1 000 cm^3 sample volumes in the presence of Septonex® or Sterinol® surfactants (*cf*. Table V). Similarly, the recovery higher than 90% was earlier reported for Au(III) under similar conditions[17].

Effect of Foreign Ions

No interference of 0.02–1 mol dm^{-3} of chloride, nitrate, sulfate or 200 mg dm^{-3} of Fe(III), Ca^{2+}, Mg^{2+}, Na^+, K^+ and 1 000 mg dm^{-3} of Al(III) was observed, when 10–20 μg of PGMs and Au(III) were retained on Separon™ SGX RPS

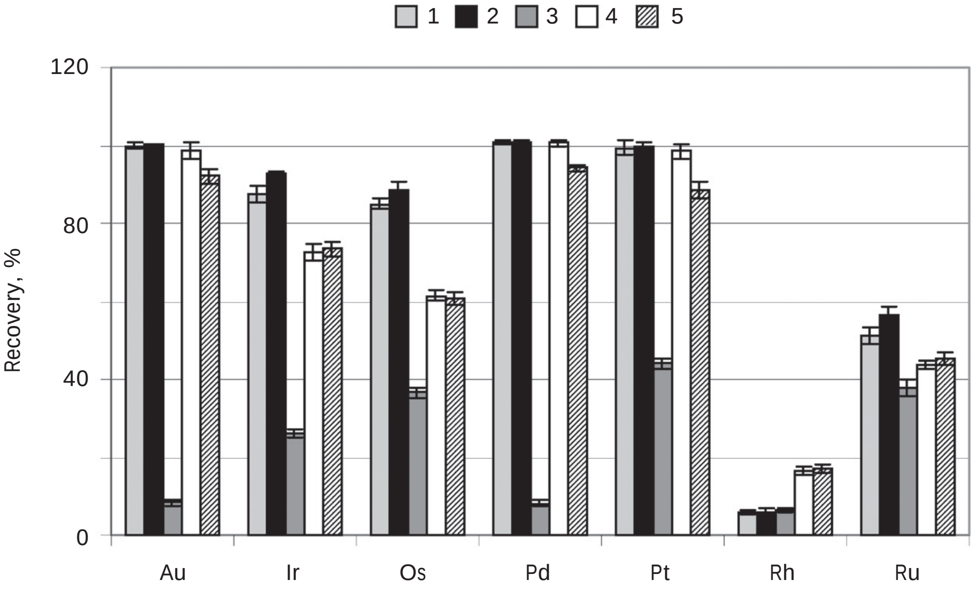

FIG. 3
Comparison of the recovery of PGMs and Au(III) after sorption on various sorbents in the presence of cationic surfactant Septonex®. An amount of 20 μg of PGMs and Au(III) was sorbed from 50 cm^3 solution containing 0.1 M HCl and 0.006 M Septonex® on LiChrolut™ RP-18 (1), LiChrolut™ RP-18e (2), LiChrolut™ EN (3), Amberlite™ XAD4 (4) and Amberlite™ XAD2 (5). An amount of 10 cm^3 acetonitrile was used for elution. The segments correspond with the confidence interval from 3 experimental values

from 50 cm^3 of a sample solution containing 0.1 M HCl and 0.006 M Septonex®.

Preconcentration of PGM and Au from Their Bromo Complexes

Similar results to the recovery of chloro complexes of PGMs and Au(III) were obtained for bromo complexes under analogous conditions. 0.006 M Septonex® and 0.1 M HBr were optimum concentrations for the sorption of 20 μg of bromo complexes of PGMs and Au on Separon™ SGX C18 from 50 cm^3 of a sample solution (Table VI). There is no preference of bromo complexes to chloro complexes of PGMs and Au for the retention.

In fact, bromo complexes of some PGMs were successively used for the separation and determination of μg cm^{-3} concentrations of Pt(II), Pt(IV), Pd(II) and Au(III) by reverse phase HPLC on octadecyl silica in the form of bromo complex associates with selected cationic surfactants[20,26]. The sorption of Pt(IV) in the form of some kind of bromo complex on octadecyl silica Separon™ SGX RPS at pH 3 is effective even for the concentration of

TABLE V
Average recovery (in %) of PGMs and Au(III) after sorption on Separon™ SGX RPS from various sample volumes[a]

Volume cm^3	Surfactant	ng cm^{-3} PGMs	Au	Ir	Os	Pd	Pt	Rh	Ru
50	A	200	100	99	75	100	99	11	23
	B	200	99	84	95	98	96	10	54
100	A	100	101	92	68	100	98	8	23
	B	100	102	79	88	100	98	5	54
250	A	40	101	89	63	100	96	2	19
	B	40	102	68	64	101	89	2	49
500	A	20	99	84	58	100	96	1	9
	B	20	102	58	52	101	89	1	45
1 000	A	10	98	73	44	99	96	0	6
	B	10	101	49	49	101	91	1	44

[a] The solution contained 0.1 M HCl and 6 cm^3 of 0.1 M Septonex® (A) or 3 cm^3 of 0.1 M Sterinol® (B). Average recoveries were calculated from 3 independent experiments.

2 ng cm^{-3} from 10–200 cm^3 sample volume[12] but such low amount is not determinable by ICP-AES.

Sorption on Amberlite™ XAD2 and XAD4

Macroporous sorbents Amberlite™ XAD2 and XAD4 strongly bind PGMs and Au(III) from their chloro complexes in solutions containing 0.1 M HCl and 0.006 M Septonex® and their desorption is difficult with ethanol, 0.5 M thiourea in 0.2 M HNO_3 or 0.2–5 M HNO_3. Acetonitrile remains the most effective eluent for Au(III), Pd(II) and Pt(IV) which leads to nearly 100% recoveries. There is, however, no preference of these sorbents to modified silica for the previous separation of PGMs and Au(III) (Fig. 3). On the contrary, no retention of PGMs and Au was observed when no cationic surfactant was used with this kind of sorbents.

Retention of PGMs and Au(III) Chloro and Bromo Complexes on Silica-Based Anion Exchanger in the Absence of Surfactant

For elution of PGMs and Au(III) from silica-based anion exchanger Separon™ SGX AX, sodium perchlorate and mineral acids were used. Recoveries for various eluents are summarised in Table VII. An amount of 2–4 cm^3 of 0.5–1 M $NaClO_4$ leads to a quantitative elution of Pd(II). 5 M HNO_3 is the optimum agent for the elution of chloro complexes of Ir(IV), Pd(II) and Pt(IV). Decreased recoveries for Au(III), Os(VI) and Ru(IV) correspond with the strong retention on the sorbent. No difference is observed in the behaviour of PGMs and Au(III) bromo complexes under similar conditions.

TABLE VI
The sorption efficiency of bromo complexes of PGMs and Au(III) on Separon™ SGX C18[a]

Metal	Au	Ir	Os	Pd	Pt	Rh	Ru
Recovery, %	101.6 ± 1.2	92.5 ± 2.1	75.7 ± 2.0	100.6 ± 2.4	98.4 ± 1.8	27.7 ± 3.1	76.9 ± 2.5

[a] PGMs and Au(III) (20 μg) were retained on Separon™ SGX C18 from 50 cm^3 solution in the presence of 0.006 M Septonex® and 0.1 M HBr. Confidence intervals were calculated at the level of significance $\alpha = 0.05$ from 6 independent repetitions.

Effect of Humic Acid

The sorption efficiency for Pt(IV), Pd(II) and Au(III) on modified silica sorbents was tested in the presence of various amounts of standard humic acid 244 MAR; the results are collected in Table VIII. The anion exchanger Separon™ SGX AX is more effective for the preconcentration of Pt(IV) and Pd(II) from humic acid-containing waters. Increased amounts of humic acids negatively influence their retention from natural waters when octadecyl silica has been used as sorbent. Moreover, the acids are partly cosorbed under above conditions and finally eluted with the used eluents.

Determination of Pt(IV), Pd(II) and Au(III) in Spiked Soil Extracts, Power Station Dust and Natural Waters Using Octadecyl Silica and Septonex® prior to ICP-AES

Spikes of PGMs and Au(III) solutions were added to 75 cm^3 of soil extracts in *aqua regia* to reach the final concentration of 0.1 mg dm^{-3} and the solutions were equilibrated for 24 h. The spiked extracts (75 cm^3) with 0.1 M Septonex® were diluted to 200 cm^3. Three aliquots of 50 cm^3 of this solution containing 0.006 M Septonex® were applied onto a cartridge with Separon™ SGX RPS and the metals were eluted with 10 cm^3 of acetonitrile and analysed by ICP-AES after solvent evaporation in the presence of 0.1 M

TABLE VII
Average recovery (in %) of PGMs and Au(III) from Separon™ SGX AX after elution with various eluents[a]

Eluent	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
0.5 M $NaClO_4$	21.1 ± 2.2	86.3 ± 1.8	51.3 ± 1.8	100.2 ± 1.8	86.4 ± 2.1	31.1 ± 1.7	40.2 ± 2.2
1 M $NaClO_4$	18.9 ± 1.7	87.1 ± 1.5	55.0 ± 3.1	100.0 ± 1.5	83.1 ± 2.4	31.9 ± 1.5	37.7 ± 2.1
1 M HCl	42.2 ± 2.6	100.3 ± 1.2	51.2 ± 3.3	100.1 ± 0.6	99.7 ± 1.2	25.5 ± 1.8	61.8 ± 2.2
5 M HCl	40.5 ± 2.2	100.9 ± 0.9	52.3 ± 1.6	101.2 ± 1.0	100.9 ± 0.9	26.2 ± 2.3	64.0 ± 2.2
5 M HNO_3[b]	70.5 ± 1.1	100.2 ± 1.2	73.5 ± 1.1	100.5 ± 0.7	100.3 ± 1.2	41.3 ± 1.1	58.4 ± 0.8
5 M HNO_3[b,c]	70.9 ± 1.9	98.5 ± 2.3	72.2 ± 1.8	100.1 ± 1.0	100.4 ± 1.7	40.2 ± 2.8	65.2 ± 1.4

[a] Sample solution (50 cm^3) contained 20 μg of PGMs and Au(III) as chloro or bromo complexes and 0.1 M HCl (HBr). Confidence intervals were calculated at the level of significance $\alpha = 0.05$ from 3 independent repetitions. [b] Confidence intervals were calculated from 6 independent repetitions. [c] Bromo complexes.

HCl (Table IX). It was observed that the twice or three times diluted *aqua regia* does not negatively influence the sorption efficiency of the sorbent for PGMs and Au but the lifetime of column filling is decreased.

For power station dust, four aliquots of a 0.2500-g sample were spiked with dilute standard solutions to contain 5 µg of PGMs and Au(III). The mixture was homogenised, dried, ignited and leached with 12 cm^3 of *aqua regia* by boiling under reflux for 1 h. After evaporating excess of acids and cooling, the mixture was filtered with a cellulose filter into a 50-cm^3 volumetric flask, the Septonex® solution was added to the final concentration of 0.006 mol dm^{-3}, filled with distilled water up to the mark and transferred onto a modified silica Separon™ SGX RPS column. The eluate in acetonitrile was analysed by ICP spectrometry after removing the solvent. The recoveries of PGMs and Au agree with those of pure dilute standard solutions. The results are collected in Table IX.

Two procedures were used for river- and humic acid-containing waters, (i) 50 cm^3 aliquots of river- or peat moor-water containing humic acid were spiked with 10 µg of PGMs and Au(III), 0.003 M Sterinol® and 0.1 M HCl and the solutions obtained were treated with Separon™ SGX RPS, eluted

TABLE VIII
Sorption efficiency (in %) on Separon™ SGX RPS and Separon™ SGX AX in the presence of humic acid 244 MAR

Sorbent	Humic acid mg dm^{-3}	Metal		
		Au	Pd	Pt
Separon™ SGX RPS[a]	10	101.0 ± 0.5	100.6 ± 0.4	98.9 ± 1.9
	50	100.2 ± 0.4	98.5 ± 1.7	97.1 ± 1.7
	100	92.3 ± 1.9	91.2 ± 2.6	88.8 ± 1.7
Separon™ SGX AX[b]	10	70.1 ± 1.5	100.3 ± 0.8	100.2 ± 2.3
	50	65.1 ± 1.3	100.1 ± 1.9	100.0 ± 1.0
	100	67.2 ± 1.3	99.9 ± 1.1	98.9 ± 1.7

[a] Pt(IV), Pd(II) and Au(III) (20 µg) were retained from 50 cm^3 solution in the presence of 0.003 M Sterinol®, 0.1 M HCl and humic acid. An amount of 10 cm^3 of ethanol was used for elution. [b] Pt(IV), Pd(II) and Au(III) (20 µg) were retained from 50 cm^3 solution in the presence of 0.1 M HCl and humic acid. An amount of 10 cm^3 of 5 M HNO_3 was used for elution. Confidence intervals were calculated at the level of significance $\alpha = 0.05$ from 3 independent repetitions.

with 10 cm^3 of ethanol and analysed on an ICP spectrometer after removal of solvent by evaporation with 0.1 M HCl, or (ii) the Separon™ SGX AX anion exchanger was used for 50-cm^3 samples of river- or peat moor-water with 10 µg PGMs and Au(III) spikes in 0.1 M HCl. The elution followed with 10 cm^3 of 5 M HNO_3 and the eluate was analysed by ICP-AES after removing excess of acid by evaporation. The results are given in Table IX.

TABLE IX
Recoveries (in %) of Au(III), Pd(II) and Pt(IV) from spiked soil extracts, power station dust and river-water after retention on Separon™ SGX RPS or Separon™ SGX AX

Sample	Sorbent[a]	Metal		
		Au	Pd	Pt
Soil extract	A	101.0 ± 1.3	95.8 ± 1.5	101.7 ± 1.2
Power station dust	A	98.8 ± 1.9	100.2 ± 0.5	99.1 ± 0.9
River water	A	98.1 ± 1.3	97.9 ± 0.6	100.7 ± 1.1
River water	B	70.3 ± 1.6	100.2 ± 1.5	100.0 ± 1.0
Humic water	A	93.0 ± 0.6	90.4 ± 1.3	88.2 ± 2.2
Humic water	B	68.5 ± 1.0	100.7 ± 0.9	98.8 ± 0.7

[a] Separon™ SGX RPS (A), Separon™ SGX AX (B). Confidence intervals were calculated at the level of significance $\alpha = 0.05$ from 3 independent repetitions.

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REFERENCES

1. *Platinum, Environmental Health Criteria 125*. World Health Organization, Geneva 1991.
2. Zereini F., Alt F.: *Anthropogenic Platinum-Group Element Emission*. Springer, New York 1999.
3. Pyrzynska K.: *Talanta* **1998**, *47*, 841.
4. Alt F., Banbauer A., Hoppstock K., Mergler B., Tölg G.: *Fresenius' J. Anal. Chem.* **1993**, *346*, 693.
5. Kummerer K., Helmers E.: *Sci. Total Environ.* **1997**, *193*, 179.
6. Bouška V., Jakeš P., Pačes T., Pokorný J. (Eds): *Geochemie*. Academia, Praha 1980.
7. Kuzmin N. M., Kubrakova I. V., Pukhovskaya V. M., Kudinova T. F.: *Zh. Anal. Khim.* **1994**, *49*, 182.
8. Paukert T.: *Chem. Listy* **1993**, *87*, 8.

9. Balcerzak M.: *Analyst (Amsterdam)* **1997**, *122*, 67R.
10. Vlašánková R., Sommer L.: *Chem. Pap.* **1999**, *53*, 200.
11. Otruba V., Strnadová M., Skalníková B.: *Talanta* **1993**, *40*, 221.
12. Vlašánková R., Otruba V., Bendl J., Fišera M., Kanický V.: *Talanta* **1999**, *48*, 839.
13. Perry B. J., Barefoot R. R., Van Loon J. C.: *Trends Anal. Chem.* **1995**, *14*, 388.
14. Parent M., Vanhoe H., Moens L., Dams R.: *Fresenius' J. Anal. Chem.* **1996**, *354*, 664.
15. Gomez M. B., Gomez M. M., Palacios M. A.: *Anal. Chim. Acta* **2000**, *404*, 285.
16. Kanický V., Otruba V., Mermet J. M.: *Talanta* **1999**, *48*, 859.
17. Hájková J., Kanický V., Otruba V.: *Collect. Czech. Chem. Commun.* **2000**, *65*, 1848.
18. IUPAC: *Compendium of Analytical Nomenclature, Definitive Rules 1997*. Blackwell Science, Oxford 1998.
19. Ginzburg S. I., Ezerskaya N. A.: *Analiticheskaya Khimiya Platinovykh Metallov*, p. 49. Nauka, Moscow 1972.
20. Doležal J., Sommer L.: *Collect. Czech. Chem. Commun.* **1997**, *62*, 1029.
21. Zbíral J.: Personal communication.
22. Dean R. B., Dixon W. Y.: *Anal. Chem.* **1951**, *23*, 636.
23. Adamson M. G.: *J. Chem. Soc. A* **1968**, 1370.
24. Adamson M. G.: *Aust. J. Chem.* **1967**, *20*, 2517.
25. Brigdes K. L., Chang J. C.: *Inorg. Chem.* **1967**, *6*, 619.
26. Sommer L., Vlašánková R.: *Chromatographia* **2000**, *52*, 692.

Příloha 5

KOSAROVA, H., **KOMENDOVA R.*** a SKERIL R.
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DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF PLATINUM IN URBAN DUST IN THE AGGLOMERATION OF BRNO, CZECH REPUBLIC

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ABSTRACT

This paper deals with conditions for pre-concentration and determination of platinum in airborne dust. Octadecyl-modified silica gel was tested for solid phase extraction to pre-concentrate platinum. The ion associates made from platinum chloro complexes with the cationic surfactant Septonex® (carbethoxy pentadecyl trimethylammonium bromide) were sorbed on modified silica gel (in the presence of 0.1 mol.L^{-1} HCl). The retained amount of platinum was eluted with acetonitrile. Recovery values of platinum from the model solution exceeded 90%. Platinum in the eluate was determined by atomic absorption spectrometry with electro thermal atomization (ET-AAS). Samples of airborne dust particulates from filters were decomposed in *aqua regia* by microwave extraction. This work published yearly monitoring values of platinum content in airborne particulate matter in Brno agglomeration, which was determined for each month. Platinum concentration ranged between 2.3–51.5 pg.m^{-3} in air, which corresponds to 61.9-2997.7 ng.g^{-1} in airborne dust.

KEYWORDS: Platinum, atomic absorption spectrometry, solid phase extraction, airborne dust

1. INTRODUCTION

The use of platinum in automotive catalysts is one of the main reasons why the environment is polluted by platinum group elements, especially by platinum, palladium and rhodium. The concentration of platinum group elements strongly increased both road dust and airborne particulates [1], but also that in soils [2] and plants [3] near the frequented roads in the last 20 years because of the introduction of catalytic converters in the Czech Republic, in 1993. Result of environmental pollution by platinum is its bioaccumulation in living organisms [4]. Platinum is generally known for its allergenic effects, for example asthma, indisposition, dermatitis and other health problems of people [4]. From the toxicological aspect, there are biologically the most available soluble species of PGE (platinum group elements), which can influence organisms and plants directly. Other risks of health are from inhaled PGE, which are parts of particles in polluted air dust. Particulates with average 2.5 μm are for human health the higher risk than particulates of 10 μm size. It is 30-57 % from total measured platinum in catch on this fraction [5]. The ultrafine particulates increase effects of this metals, and it affords a big reaction area per unit weight lung [6]. The amount of platinum in urine depends on frequency of traffic in the city [7]. Acute toxicity of platinum depends on kind of compound, when soluble compounds are the most toxic ones. For example, PtO_2 is relatively high-toxic (LD_{50rat} >8000 mg.kg^{-1}), and Na_4 [$PtCl_6$] is mild toxic (LD_{50rat} 25-50 mg.kg^{-1}) [8]. The amount of platinum in the environment is so low, if more as the acute toxicity can show chronic toxicity effects. Reaction of platinum with other compounds in the environment (for example humic acids) can cause higher health risk due to increased soluble, bioavailable and more toxic forms. The highest risk represents fine air dust.

Platinum is emitted from catalysts, mainly in form of oxides. Approx. about 10% from all emissions of platinum from catalyst convectors are soluble in water [9]. The amount of soluble Pt in airborne dust is 30–43%, while it is only 2.5–6.9% in tunnel dust. Solubility of platinum in water extensively affected acute toxicity. Soluble compounds of platinum are PtO, PtO_2 and $PtCl_2$. In rain water is platinum the most soluble, but at pH 1 and pH 3-9, the solubility of platinum is lower. In a mixture of pluvial water with soil, solubility of platinum is lower than in pluvial water alone. The next factor, which can affect solubility of platinum, is size of emitted particulates. With decreasing size of particulates, the solubility is higher. For instance, the particulates with averaged 3.4 nm are soluble (22%), while solubility of those with an average of 25 nm is only 2%, because activated energy for oxidation small particulate is lower [10].

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Emission of platinum is affected by fast alternation oxide-reducing conditions, high operation temperature and, subsequently, mechanical abrasion [11]. Noble metals are applied on reaction areas constituted of mild steel and a layer of γ-Al_2O_3. The catalytic layer is mainly composed of 90% γ-Al_2O_3, and different additives, such as oxides of metals Ce, Zr, La, Ni, Fe, Ti, etc. Catalytic layer of platinum is applied in form of $H_2[PtCl_6$ [12]. When the operating temperature of convector is high, the porous layer of γ-Al_2O_3 is destroyed and originated the α-form, which is nonporous and simultaneously originated oxides of platinum [12].

This research is based on determination of platinum in airborne particulate matter in time intervals of 1 year (from 1.11. 2012 to 30.10. 2013) near frequent roads in Brno agglomeration, in view of negative effects of platinum for living organisms in the environment and human health in urban areas.

2. MATERIALS AND METHODS

2.1 Instruments and equipment

Platinum in model solutions and samples was measured by atomic absorption spectrometry with an electrothermal atomization ET-AAS ZEEnit 60 unit (Analytik Jena AG) with Zeeman correction background and with autosampler. The atomic absorption spectrometer was equipped with graphite furnace and a platinum hollow cathode lamp by Photron, Australia. The current used for the platinum lamp was 8 mA. Optimized conditions of the temperature program for measuring the absorption signal were: first step of drying at 90 °C for 20 sec, second step drying at 105 °C for 20 sec, and third step of drying at 110 °C for 10 sec, pyrolysis at 1600 °C for 10 sec, atomization at 2300 °C for 8 sec and cleaning at 2400 °C for 4 sec. Other conditions of measurement were slit width 0.2 nm, wavelength 265.9 nm, and injection volume 20 μl.

Platinum was pre-concentrated by SPE (solid phase extraction) procedure. The sorption equipment was composed as follows: the pump PCD 82.4 K with 4 cartridges ISMATEC ISO 649, the silicon tubes, the columns Bond Elut-C18 (500 mg, 3 ml) from Agilent, and the vacuum system BAKER J. T. spe-12G vacuum processor.

Sorption process consisted of 4 steps - the conditioning of the sorbent, sorption sample, washing of the sorbent, and elution of the analyte. The silica gel C18 conditioned by solution consisted of 0.005 mol.L^{-1} Septonex® in 0.1 mol.L^{-1} HCl, and was used for sorption using successfully acetonitrile as eluent.

The samples were decomposed by a microwave extractor Mileston Digestion/Drying mls 1200 with carousel, with 6 extraction thimbles from Teflon™. The program for decomposition of samples consisted of 5 steps: 200 W for 2 min, 400 W for 2 min, 0 W for 5 min, and 600 W for 10 min, and cooling for 20 min.

2.2 Chemicals

All used chemicals were of analytical-grade purity. Certified reference material, and an aqueous calibration solution of platinum with concentration 1±0.002 g.L^{-1} in 5% HCl (Czech metereological institute, ASTASOL®, Analytica s.r.o., Prague, Czech Republic) were used for the optimization method to determine platinum. In this research, 3 cationic surfactants were tested (Septonex® - carbaetoxypentadecyltrimethylammonium bromide $C_{21}H_{44}O_2NBr$ (GBN a.s., Prague, Czech Republic), Zephyramin® - benzyldimethyltetradecylammonium chloride $C_{23}H_{42}NCl$ (Sigma Aldrich, Steinheim, Germany), and Ajatin® - benzyldimethyldodecylammonium bromide $C_{21}H_{38}NBr$ (Sigma Aldrich, Steinheim, Germany). All used solutions were kept in acidic medium to prevent sorption platinum on the volumetric glassware wall. A solution of 0.1 mol.L^{-1} HCl was prepared from concentrated HCl (Analytica s.r.o., Prague, Czech Republic). The samples were decomposed in *aqua regia*, made from HCl and nitric acid (Penta, Chrudim, Czech Republic) in a ratio of 3:1. Absolute ethanol and acetonitrile (Penta, Chrudim, Czech Republic) were tested as elutents. The other used chemicals were from Lachema (Brno, Czech Republic), Merck (Darmstadt, Germany), and Sigma Aldrich (Steinheim, Germany).

2.3 Characteristics of samples

The glass microfiber filters GF/C Whatman were used for sampling air dust and, furthermore, for analysis. The filters were situated in the air sampler DHA-80 by firm Digitel Elektronik belonging to the Czech Hydrometeorological Institute. The air sampler was located on the street Údolní in Brno (49°11'53.132"N, 16°35'37.142"E). This main road has 3 lanes, and cars ride stop-start here in the rush hour. It has been proven that higher amounts of Pt particulates from convector to air in this style of driving were released. Samples were procured continually every 24 h from 1.11.2012 to 31.10.2013. The filters were weighed to determine the exact adherent dust and stored to to insulate the polymer cover.

3. RESULTS AND DISCUSSION

3.1 Optimization of measurement on ET-AAS

For preparation of this method, first of all, the temperature of pyrolysis was optimized (from 900 to 1800 °C, with steps of 100 °C (see Fig. 1). Absorption signal was greatest at 1600 °C. Equally, the temperatures for optimized atomization extent were 2000, 2100, 2200, 2300 and 2350 °C, and 2300 °C was used for the next measuring.

There was used a slit width of 0.2 nm for optimized conditions. Expansion of this slot was accompanied by more background noise and reduced peak area. The current supplied to the lamp was 8 mA. The signal decreased when this current was changed.

The calculated values from calibration curve for LOD (limit of detection) was 1.137 μg.L^{-1} and for LOQ (limit of quantification), it was 3.791 μg.L^{-1}.

Further, the effect of acidity on signal of platinum was evaluated. HCl was used for this experiment, and its concentration was tested for values of 0.001, 0.01, 0.05, 0.1, 0.2, 0.5 and 0.9 mol.L^{-1}. The concentration of 0.1 mol.L^{-1} and higher concentrations do not affect negatively the signal of platinum. The 0.1 mol.L^{-1} HCl level was used during the measurement and for preparing all solutions.

The effect of the concentration of surfactant Septonex® was also tested (Fig. 3). Surfactants are generally surface-active matters. The monomeric dissociated form is present in solution if the concentration of the surfactant in solution is small. This form can create ion associates with opposite charged ions. Thirteen solutions of Septonex® were tested in a concentration range from 1.10^{-5} to 1.10^{-2} mol.L^{-1}. The lowest point on Fig. 3 shows the critical micellar concentration of Septonex®. The surfactant creates micelles at this concentration. This micellar phase stabilizes the formation of ion associates. The concentration of 5.10^{-3} mol.L^{-1} had the weakest effect on the absorption signal of platinum. Therefore, this concentration was used in all our experiments.

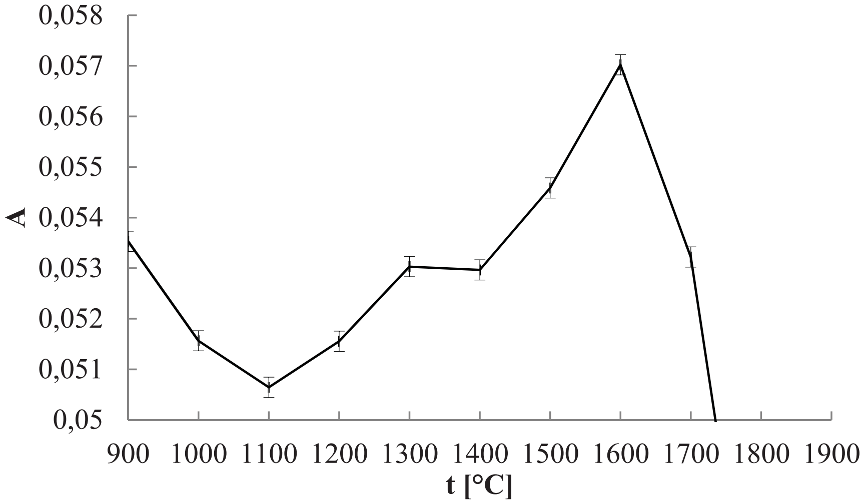

FIGURE 1 - Optimization of temperature of pyrolysis.

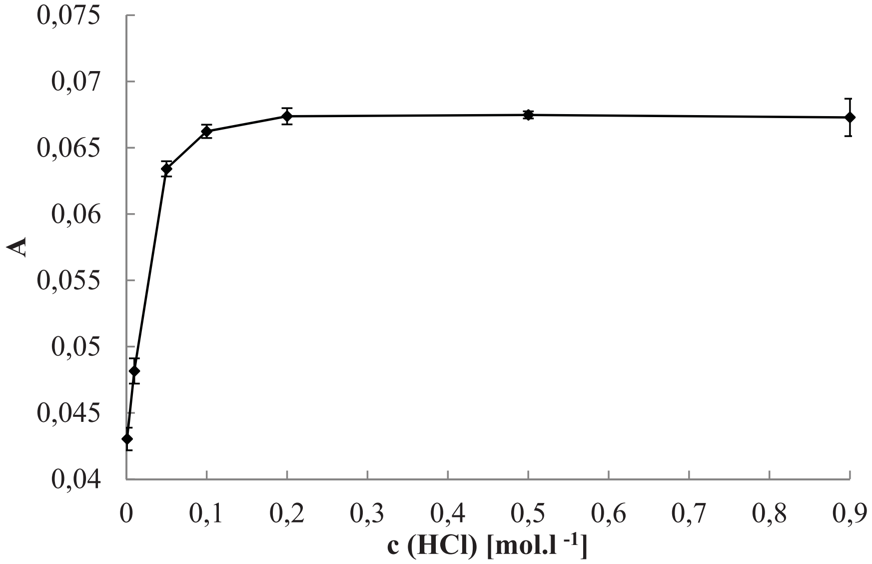

FIGURE 2 - Effect of acidity on Pt absorption signal.

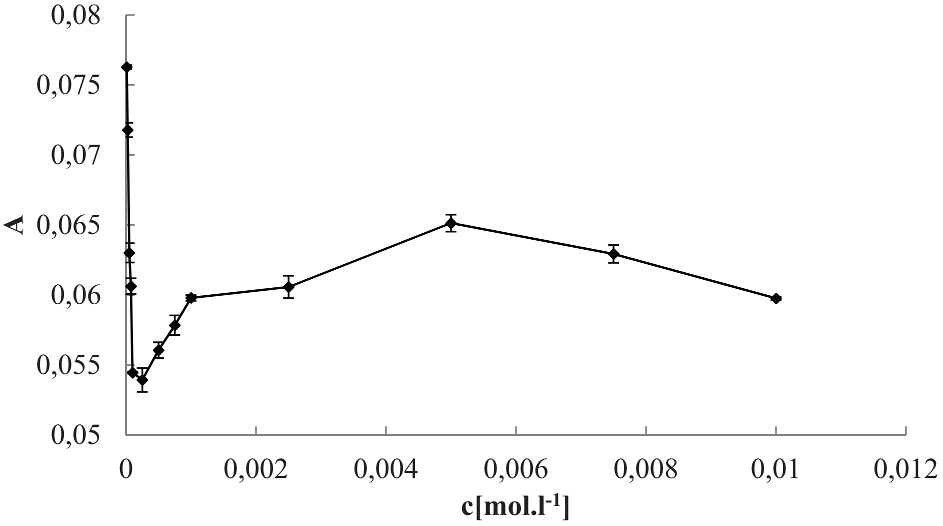

FIGURE 3 - Effect of concentration of Septonex® on Pt absorption signal.

For detecting interferences, the effects of some ions were tested (Mn^{2+}, Al^{3+}, Fe^{3+}, NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-}, HCO_3^- and NO_3^-). For every ion, 3 solutions were prepared separately, and abundance was compared to platinum in the ratios 100:1, 1000:1 and 2500:1. None of the tested ions disturbed platinum absorption signal.

3.2 Optimization of SPE preconcentration

The principle of sorption was the separation of platinum on the basis of formation of the ionic associates, when the cationic surfactant Septonex® reacted with the chloro complex of platinum. The chloro complex of platinum is bound to the ammonium ions in the structure of Septonex®, and interacted together with a solid sorbent [13].

For sorption, 2 kinds of column were tested: Strata C18-E and Agilent Bond Elut C18. Common carbon chain contains –OH groups, which are in the Strata columns replaced by shorter hydrocarbon chains (e.g. methyl, trimethyl). This was the reason why the sorption of platinum on this column was not quantitatively. Maximum efficiency of pre-concentration of platinum was only 43% on Strata column, and on Agilent column, it was 93%. Silica gel modified of octadecyl with -OH groups was preferable for pre-concentration of platinum.

The ability of surfactants to form ionic associates and, therefore, their ability to increase efficiency of pre-concentration of platinum is different, due to their different structures. Under this aspect, the best properties have surfactants with long alkyl and ramified chains. Pre-concentration is more efficient with increasing length and ramification chain. We tested 3 surfactants - Septonex®, Ajatin® and Zephyramin® (concentration 0.005 mol.L^{-1} for all surfactants). Ajatin® and Zephyramin® have very similar structures and so, their results were almost the same. The averaged efficiency pre-concentration of platinum with Ajatin® was 68% and with Zephyramin® 71%. Septonex® has a more ramified structure, and so, the efficiency of pre-concentration for platinum was 96 %, on average. The Septonex® was used as sorbent-conditioning agent, but if it was added to the solution containing platinum, efficiency of pre-concentration was higher. Therefore, it was used for all tested surfactants.

As in ETA-AAS, the effect of acidity on pre-concentration of platinum was tested. HCl was used for tests (concentrations of 0.001, 0.01, 0.05, 0.1, 0.5 and 1 mol.L^{-1}). The efficiency of pre-concentration was not lower than 70 %, and for the concentration of 0.1 mol.L^{-1}, efficiency was 96%, on average.

Further experiments are necessary to test eluting agents (ethanol, acetonitrile and mixtures of ethanol-acetonitrile, ethanol-HCl, acetonitrile-HCl and ethanol-acetonitrile-HCl were tested). Acetonitrile as eluent achieved the best results. The efficiency of desorption was about 96 %.

3.3 Analysis of real samples of airborne dust

Altogether, we analysed 365 air filters. These filters were sequentially placed in the aerosol sampler DHA-80 in which dust from air was collected. Filters were leached by *aqua regia* in the microwave extractor. Platinum was determined in a mixed sample, which consisted of 30 air filters. Platinum was determined for each separate month, and optimal SPE and ET-AAS conditions were identified. All specified concentration values of platinum in real samples were above the limit of detection (1.137 μg.L^{-1}). Only the value of November was under the limit of quantification (3.791 μg.L^{-1}).

The observed concentrations of the platinum in the airborne particulate matter from Brno's agglomeration (Fig. 4) were in the interval of 61.9 – 2997.7 $ng.g^{-1}$ in dust, and in the interval of 2.3-51.5 $pg.m^{-3}$ in air (Fig. 5). Concentration of the platinum in the airborne particulate matter depended on the season. It is interesting that the amount of platinum is increasing with decreasing amount of air dust, and conversely (Fig. 4). The higher amount of platinum in summer months can be affected by worse dispersion conditions and higher atmospheric moisture. With real samples, blanks were measured, but no platinum was found on these filters.

Limbeck et al. [14] also dealt with determination of PGE in airborne particulate matter in in Klagenfurt and Salzburg (Austria). They used absolutely the same appliance for sampling and they had similar results as in this Brno thesis. The method used for analysis was ETA-AAS too.

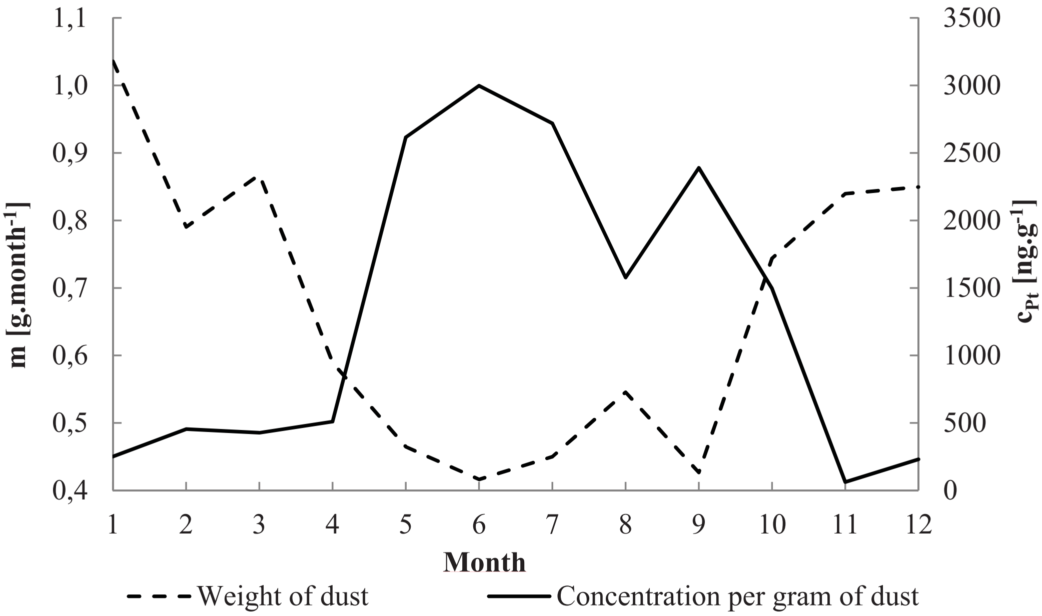

FIGURE 4 - The determined amount of Pt in dependence on the weight of dust and month of the year.

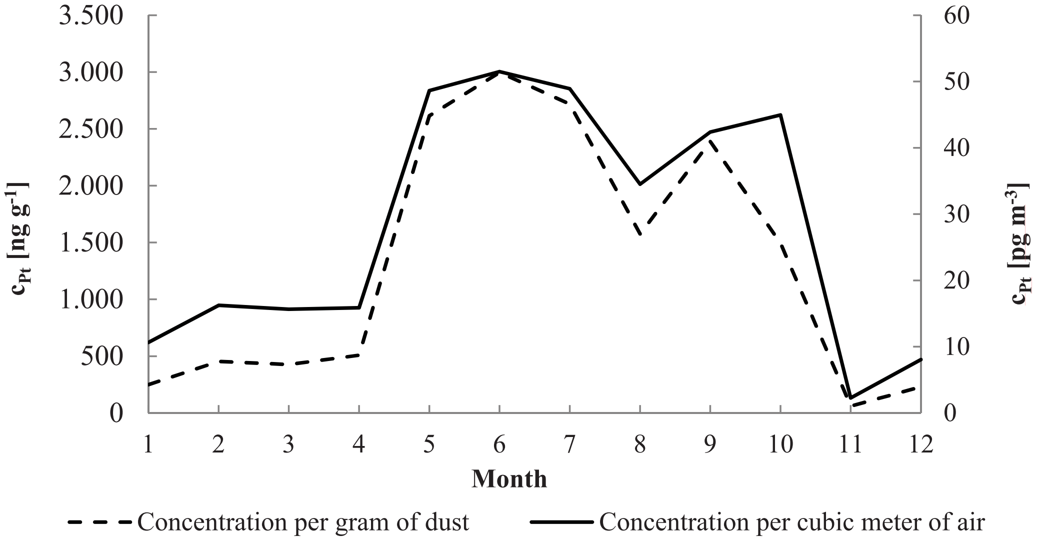

FIGURE 5 - The determined amount of Pt in dependence on the weight of dust and the volume of air.

Vlašánková et al. [15] dealt with pre-concentration of PGE on modified silica gel, and they determined, by inductively coupled plasma mass spectrometry in airborne particulates, values of platinum in samples in the interval 13–42 pg.m^{-3}. These results are similar to our amounts of platinum too.

4. CONCLUSION

Optimized conditions for SPE and ETA-AAS were applied for the analysis of platinum in airborne dust. Platinum was separated and pre-concentrated on octadecyl-modified silica gel sorbent in the form of ion associates with cationic surfactant. The glass micro fibre filters were analysed from samplings of airborne dust in Czech Hydrometeorological Institute. All samples of air dust were sampled in the city of Brno from 1.11.2012 to 30.10.2013 on the intersections Údolní and Úvoz (49°11'53.132"N, 16°35'37.142"E). The determined amounts of platinum were in the interval of 61.9-2997.7 ng.g^{-1} in dust, and in the interval of 2.3-51.5 pg.m^{-3} in air.

These values obtained for platinum content in fly-ash dust confirm its increasing amount in the environment, particularly in air and dust of large urban areas with high traffic density. The increasing amount of platinum from automotive catalysts can cause serious health problems for sensitive persons, because of their allergenic properties. It is, therefore, highly necessary to have an overview of the platinum concentrations in various environmental compartments, due to knowledge and the possible negative effects, and also to determine their cycles in the environment.

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REFERENCES

[1] Wichmann, H., Bahadir, M. (2001) Determination of the noble metals platinum, rhodium, and palladium in airborne particles. Fresenius Environmental Bulletin 10, 106-108.

[2] Angelone, M., Armiento, G., Cinti, D., Somma, R., Trocciola, A. (2002) Platinum and heavy metal concentration levels in urban soils of Naples (Italy). Fresenius Environmental Bulletin 11, 432-436.

[3] Papa, S., Bartoli, G., Di Martino, D., Fioretto, A. (2010) Occurrence of platinum in the leaves of holm-oak (*Quercus ilex L.*) from different sites (streets and squares) in the city of Caserta (Italy). Fresenius Environmental Bulletin 19, 2109-2115.

[4] Ravindra, K., Bencs, L., Van Grieken, R. (2004) Platinum group elements in the environment and their health risk. Science of The Total Environment 318, 1-43

[5] Wiesman, C.L.S, Zereini F. (2009). Airborne particulate matter, platinum group elements and human health: A review of recent evidence. Science of The Total Environment 407, 2493-2500

[6] Wilson, M.R., Lightbody, J.H., Donaldson, K., Sales, J., Stone, V. (2002) Interactions between Ultrafine Particles and Transition Metals *in Vivo* and *in Vitro*. Toxicology and Applied Pharmacology 184, 172–179

[7] Wang, Y., Li, X. (2012) Health Risk of Platinum Group Elements from Automobile Catalysts. Procedia Engineering 45, 1004–1009

[8] Rosner, G., König, H.P., Coenen-Stass, D. (1991) Environmental Health Criteria 125: Platinum. Geneva: World Health Organization

[9] Moldovan, M., Palacios, M.A., Gómez, M.M., Morrison, G., Rauch, S., McLeod, C., Ma, R., Caroli, S., Alimonti, A., Petrucci, F., Bocca, B., Schramel, P., Zischka, M., Pettersson, C., Wass, U., Luna, M., Saenz, J.C., Santamaŕia, J. (2002) Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. Science of The Total Environment 296, 199-208

[10] Ek, K.H., Morrison, G.M., Rauch, S. (2004) Environmental routes for platinum group elements to biological materials—a review. Science of The Total Environment 334–335, 21-38

[11] Sikorová, L., Ličbinský, R., Adamec, V. (2011) The platinum group metals from automobile catalytic converters in the environment. Chemické listy 105, 361-366

[12] Ravindra, K., Bencs, L., Van Grieken, R. (2004) Platinum group elements in the environment and their health risk. Science of The Total Environment 318, 1-43

[13] Komendová-Vlašánková, R., Sommer, L. (2002) Separation and Preconcentration of Platinum Group Metals and Gold on Modified Silica and XAD Sorbents in the Presence of Cationic Surfactants for Their Determination by ICP-AES. Collection of Czechoslovak Chemical Communication 67, 454-470

[14] Limbeck, A., Rendl, J., Heimburger, G., Kranabetter, A., Puxbaum, H. (2004) Seasonal variation of palladium, elemental carbon and aerosol mass concentrations in airborne particulate matter. Atmospheric Environment 38, 1979–1987

[15] Vlašánková, R., Otruba, V., Bendl, J., Fišera, M., Kanický, V. (1999) Preconcentration of platinum group metals on modified silicagel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates. Talanta 48, 839–846

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Příloha 6

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ORIGINAL PAPER

The distribution of platinum in the environment in large cities: a model study from Brno, Czech Republic

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Abstract

Due to increasing car traffic, concentrations of platinum (Pt) in all environmental compartments have significantly increased in the last two decades. Primarily, contamination of larger cities and specific environmental compartments has mostly been examined. Only limited data on Pt pollution of middle-sized cities are available. In this article, we study Pt concentrations in tunnel dust, soil and plant material collected in the middle-sized city of Brno, Czech Republic, in 2015–2016. Prior to analyses of samples, we optimized and validated preconcentration as a step preceding to AAS analysis in order to improve the LOQ and LOD values. Platinum concentration in tunnel dust ranged from 66.3 to 192 ng g^{-1} before cleaning the tunnels and from 29.2 to 38.2 ng g^{-1} after it. As expected, the Pt contents in soil and plant material were two to three orders lower. The concentrations in soil fluctuated from 10.5 to 15.7 ng g^{-1} Pt; they were comparable to Pt levels in grass that oscillated from 10.0 to 11.6 ng g^{-1} Pt. This implies relatively easy dissolution of Pt and its transport from soil to grass, which is in contrast to previous assumption that Pt is solubilized very slowly in environmental compartments. The Pt contents in all samples collected outside the traffic routes did not exceed the limit of quantification. Therefore, concentrations of Pt in the parts of the city exposed to high car traffic are several orders higher than those found in non-exposed sites; levels of Pt are increasing fast, which should initiate more comprehensive and intense research on the subject.

Keywords Atomic absorption spectrometry · Plant material · Platinum · Soil · Solid-phase extraction · Tunnel dust

Introduction

In the last two decades, levels of platinum (Pt) and its compounds in all environmental compartments have significantly increased. The main reason is rising car traffic, which is considered as one of the major sources of pollution (Wang and Li 2012). The types of environmental pollutants are progressively changing. A significant variation was induced by the ban of leaded petrol, effective in the Czech Republic since January 1, 2001, which was accompanied by the use of catalytic converters of exhaust gases. The above change triggered emissions of new pollutants such as platinum metals and their compounds. Requirements for quantitative and qualitative composition of exhaust emissions are influenced mainly by approved regulations on EURO emission limits, which restrict the concentrations of carbon monoxide, hydrocarbons, nitrogen oxides and particulate matter. These standards, however, do not apply to Pt metals emissions.

The catalytic converters are devices made for catalytic oxidation and reduction in hot toxic exhaust fumes to non-toxic or less toxic products. As a rule, platinum or alloys of palladium and rhodium are used as catalysts; the above leads to gradual abrasion of their active surface and to release of small particles of Pt metals and their compounds into the environment (Rosner et al. 1991; Spaziani et al. 2008; Dubiella-Jackowska et al. 2009; Reith et al. 2014).

In nature, emitted Pt and its compounds can virtually contaminate all environmental compartments. Their mobility and bioavailability are enhanced by their solubilization. Platinum present in road dust occurs in various forms such as oxides, chlorides or metallic Pt; their water solubility depends on pH, redox potential and presence of common metal ions and complexing agents in water. Solubility of Pt in rain water in the pH range 5–8 fluctuates between

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0.010 and 0.025%, and at pH 1, it reaches the value of about 0.5%. It was shown that presence of sulfur in soil or water positively influences solubility of Pt; there are studies which report solubility of up to 10% of Pt contained in fine dust particles (Zereini and Alt 2000; Ravindra et al. 2004). In general, solubility of particles is given by their size and chemical nature; only around 10% of the released Pt particles are rather quickly soluble in water. The rest, however, is not inert either and can be subjected to a number of slower reactions, which results again in the presence of soluble forms increasing thus mobility and bioavailability of Pt particles (Rosner et al. 1991; Bencs et al. 2011).

Even at low concentrations, solubilized Pt metals can enter the food web (Pawlak et al. 2014) and, consecutively, cause serious health problems to animals and people (Wiseman and Zereini 2009). It was shown that Pt(IV) ion with high redox potential can oxidize sulfur in side chains of proteins and denature them, thereby causing variety of problems such as reduction in integrity of cell membranes, inhibition of cell functions or changes in synthesis of other proteins.

Furthermore, many Pt complexes exhibit bactericidal effect caused by inhibition of nucleic acid synthesis and cell division (Rosner et al. 1991). Problems associated with damage of kidney glomeruli (Rosner et al. 1991) were also observed in higher organisms exposed to various doses of Pt salts. Platinum complexes containing halogen ligands belong to the most important allergens, and their aggressiveness increases with higher number of halogen atoms in the molecule. Exposure to the above complexes induces health problems such as autoimmune disorders, asthma or dermatitis (Moldovan et al. 2002; Ek et al. 2004).

As aforementioned, concentration of Pt metals in environmental compartments is progressively increasing due to high traffic. After emission of exhaust fumes, Pt comes into a direct contact with road surface, vegetation (Komendova 2018), buildings or soil that are located in immediate vicinity of roads. Concentration of Pt in road dust may reach values of about 100 ng g^{-1}; its concentration decreases with increasing distance from roads and with rising depth of the soil layer (Zereini and Alt 2000; Hooda et al. 2007; Mihaljevič et al. 2013). In general, the amount of Pt released from automotive catalysts ranges in orders of ng km^{-1} according to distance travelled; levels of pg m^{-3} were found in air close to busy roads, and Pt amounts oscillating within ng g^{-1} range were determined in road dust, soil, vegetation and bodies of animals (Zimmermann et al. 2003). Platinum is also accumulating in marine sediments. The research conducted in the 1980s reported Pt metals levels of 150 pg L^{-1} and, after two decades, their 50 times increase (Zereini and Alt 2000; Abdou et al. 2016). That means that concentration of Pt metals in environment did not exceed critical level. As a result, Pt occurring in environmental compartments has not been regarded as a substantial problem; there is only scarce information on its distribution available.

Analyses of Pt metals in environmental matrices require an approach sensitive enough to determine their trace concentrations. Therefore, either the use of a sensitive, usually costly analytical technique is required, or the samples are preconcentrated, and a less sensitive device can be used.

An ICP-MS device, whose detection limits usually range within units of ng L^{-1}, is regarded as a sufficiently sensitive instrument for Pt metals analyses. The preconcentration step is typically followed by AAS analysis, with detection limits in µg L^{-1}. Nevertheless, the preconcentration step can improve sensitivity of the above method by several orders enhancing it thus to performance shown by more sensitive analytical techniques. In addition, preconcentration process removes accompanying compounds such as other ions or natural colloids.

Direct analyses of trace amounts of Pt in biological materials (Zimmermann et al. 2003) and soils or road dust (Spaziani et al. 2008) were conducted as reported. The techniques used included ET-AAS atomic spectrometry (Leopold et al. 2008), ICP-OES, ICP-MS (Bencs et al. 2003; Niemelä et al. 2004; Goncalves et al. 2008), DRC-ICP-MS (Kan and Tanner 2004), ICP-MS/MS (Machado et al. 2017) or voltammetry (Orecchio and Amorello 2011). The advantages of separation and preconcentration techniques using solid sorbents such as solid-phase extraction (SPE) were accounted and proved in many studies (Vlašánková et al. 1999; Vlašánková and Sommer 1999; Komendová-Vlašánková and Sommer 2002; Chwastowska et al. 2004; Castillo et al. 2012; Kononova et al. 2012).

In particular, researchers (Komendová-Vlašánková and Sommer 2002) developed a procedure for separation and preconcentration of trace amounts of Pt on C18 silica gel. This method had been tested only with spiked materials. As a novelty, it was applied for determination of Pt in real soil and grass samples within this study.

As aforementioned, the steadily increasing intensity of traffic, especially in industrially developed countries, leads to a tremendous increase in concentration of Pt metals in environmental matrices. However, up to now, only little attention has been paid to the above rise. Contamination of larger cities and specific environmental compartments has mostly been examined. Only limited data on pollution of middle-sized cities are available. Therefore, the aim of this work was to (1) optimize and validate the separation and preconcentration method elaborated by Komendová-Vlašánková and Sommer for ICP-MS in 2002 to be applicable for AAS analyses using a certified tunnel dust standard and (2) use this method for determination of Pt in soil and grass samples monitoring thus volume of automobile transport in Brno, Czech Republic. Brno serves as a model of a Central European city with population of around 400 thousands inhabitants; the city has experienced a substantial increase in car traffic, industrial production and transport tunnels building in the last 20 years.

Materials and methods

Soil, tunnel dust and plant samples

Three types of samples exposed to car traffic were analyzed: soils, plant tissues and tunnel dust. Dust samples were obtained mainly from walls of tunnels and underpasses located within the city of Brno. The samples were collected in the Husovice, Pisárky and Dobrovského tunnels, each having one upward and downward tube. The tunnels are cleaned twice a year, in spring and autumn (see Table 1). They are linked to each other by connecting roads; the tunnels show traffic volume of about 40 thousand cars per 24 h. The dust settled in tunnels was collected in two steps. First sampling was carried out shortly before cleaning the tunnels; then, the second one was done a month after the cleaning. To ensure consistency of dust particles, dust in the form of powder was scraped from the walls using a broom at a height of about 1 m above the road.

Collection of soil and grass samples was carried out at several sites located in Brno, namely around the high traffic (average traffic over 40,000 cars per 24 h), medium traffic (average traffic 20,000 cars per 24 h) and low traffic roads (1000 cars per 24 h in average) lined with grass strips. The samples were collected around the following streets categorized into three above classes: high traffic streets (Svatoplukova, Zvonařka and Úvoz); medium traffic streets (Lipová, Černovická and Jedovnická); and low traffic streets (Podbělová, Barvičova and Střední). Soil, as the underneath of grass, was always sampled together with it at one sampling site situated close to the roadway. The grass was then separated from the soil, and the samples were subsequently dried at room temperature to constant weight. This process was followed by homogenization, quartering and decomposition procedures. Analyzed samples collected in the areas near the traffic-affected roads from the above three categories were compared with the samples from traffic-free locations, which were supposed to show significantly lower levels of contamination. These no traffic samples were obtained in Lužánky Park, Líšeň Calcite Quarry and Mariánské Valley (see Table 1).

Decomposition of road dust samples was carried out in a microwave extractor using *aqua regia* (HCl/HNO_3 3:1). Samples (0.25 g) were quantitatively transferred into six Teflon™ patrons and mixed with 10 mL of *aqua regia*. The cartridges were then placed in the microwave extractor and decomposed subsequently according to the program described in Table 2. After decomposition, the content of the patrons was quantitatively filtered through a glass filter. Consequently, the filtrate was evaporated in Teflon® dishes on a hot plate. Quantitative conversion of the residue to a 25-mL volumetric flask was done via addition of 0.1 mol L^{-1} HCl to avoid sorption of Pt on the vessel walls.

Decomposition of soil and grass samples was carried out using the classical wet way in a 250-mL boiling reflux flask with *aqua regia*. The sample (10 g of soil, 5 g of grass) was quantitatively transferred to a round-bottom flask, wetted with HNO_3 (15 mL) and left in it until the next day, when HCl (45 mL) was added. The processed sample solution was brought to boiling point via a heating mantle. After 2 h at reflux, water (25 mL) was added and the solution of the specimen was boiled for additional 15 min and filtered then. Subsequently, the solvent was evaporated using a hot plate and quantitative conversion of decomposed sample into a 50-mL volumetric flask filled up with 0.1 mol L^{-1} HCl was done.

Instrumentation

An atomic absorption spectrometer ZEEnit 60 (Analytik Jena, Germany) with transversely heated graphite furnace, a Zeeman background corrector, a platinum hollow cathode lamp by Photron Australia and an autosampler were used for determination of Pt. Optimal measurement parameters of temperature program are given in Table 3. The method for determination of Pt by the ET-AAS ZEEnit 60 device has extensively been studied and optimized. Used wavelength, temperature program, slit width and the effect of acidity on the signal were optimized. The effect of the Septonex®surfactant and influence of other accompanying elements contained in real samples after acid digestion have also been studied (Komendová-Vlašánková and Sommer 2002; Kosárová et al. 2015).

The values of instrumental limits obtained from calibration function measured using ET-AAS were determined as follows: Limit of detection (LOD) was calculated at 1.14 μg L^{-1} and limit of quantification (LOQ) was gained at 3.79 μg L^{-1}. All results obtained within this study are calculated as the average results of three separate independent determinations; each of them was done five times using an atomic absorption spectrometer. The resulting values of Pt content found in environmental samples are given as mass concentration (after conversion of the weight of analyzed material) in ng g^{-1}, which corresponds to volume concentration in μg L^{-1}.

Procedure

A Milestone MLS-1200 Microwave Laboratory System was used for decomposition of tunnel dust samples. Its carousel was equipped with six extraction thimbles made from Teflon™. The optimal program for decomposition of samples included five heating operation steps: 2 min at 200 W; 2 min at 400 W; 5 min at 0 W; 10 min at 600 W; and final cooling of patrons for 20 min.

The solid-phase extraction sorption system for separation and preconcentration of Pt from decomposed samples consisted of a peristaltic PCD 82.4 K pump with four ISMATEC ISO649 positions (Czech Republic), silicon tubes, SPE Bond Elut-C18 columns and a BAKER J. T. spe-12G vacuum suction device with 12 slots for location of the SPE columns.

Table 1 Characterization of sample collection sites

Sample number	Sample type	Site of sample collection	GPS
Tunnels			
1	t	Husovice tunnel, upward	49°12′59.746″N, 16°37′52.961″E
2	t	Husovice tunnel, downward	49°12′59.746″N, 16°37′52.961″E
3	t	Pisárky tunnel, upward	49°11′9.584″N, 16°33′58.241″E
4	t	Pisárky tunnel, downward	49°11′9.584″N, 16°33′58.241″E
5	t	Dobrovského tunnel, upward	49°13′7.414″N, 16°35′24.872″E
6	t	Dobrovského tunnel, downward	49°13′7.414″N, 16°35′24.872″E
7	t	Pisárky underpass	49°11′38.509″N, 16°34′9.729″E
8	t	Husovice tunnel, upward	49°12′59.746″N, 16°37′52.961″E
9	t	Pisárky tunnel, upward	49°11′9.584″N, 16°33′58.241″E
High traffic			
10	s	Svatoplukova street^{ht}	49°12′34.941″N, 16°38′32.812″E
11	g		
12	s	Úvoz street^{ht}	49°12′2.857″N, 16°35′34.972″E
13	g		
14	s	Zvonařka street^{ht}	49°11′13.378″N, 16°37′6.311″E
15	g		
Medium traffic			
16	s	Černovická street^{mt}	49°10′42.132″N, 16°38′45.299″E
17	g		
18	s	Jedovnická street^{mt}	49°12′40.931″N, 16°40′24.794″E
19	g		
20	s	Lipová street^{mt}	49°11′37.349″N, 16°34′36.931″E
21	g		
Low traffic			
22	s	Podbělová street^{lt}	49°12′50.626″N, 16°41′10.465″E
23	g		
24	s	Barvičova street^{lt}	49°11′58.021″N, 16°34′42.110″E
25	g		
26	s	Střední street^{lt}	49°12′38.491″N, 16°36′22.711″E
27	g		
No traffic			
28	s	Lužánky park^{nt}	49°12′24.419″N, 16°36′31.801″E
29	g		
30	s	Kalcit quarry^{nt}	49°13′22.881″N, 16°41′28.775″E
31	g		
32	s	Mariánské valley^{nt}	49°12′59.445″N, 16°43′9.494″E
33	g		

Each sample was labeled with a number. The samples were classified into the following categories: *t* tunnel dust, *tb* tunnel dust before cleaning, *ta* tunnel dust after cleaning, *s* soil, *g* grass. Four categories of sampling sites were distinguished: *ht* high traffic, *mt* medium traffic, *lt* low traffic and *nt* no traffic places

The sorption procedure involved four consecutive steps: (1) conditioning the sorbent; (2) sorption of the sample; (3) washing the sorbent; and (4) elution of the analyte. The octadecyl silica gel was used as a sorbent for SPE. The conditioning solution consisted of 10 mL 0.005 mol L^{-1} Septonex® in 0.1 mol L^{-1} HCl; the washing was performed with distilled water and 10 mL of acetonitrile was used as an eluent. The flow rate was set at 1 mL min^{-1}. The 95% sorption efficiency for Pt was confirmed through SPE optimization process in model solutions. Interferences of elements were not observed, because they were eliminated during the separation procedure.

Reagents

Platinum certified reference material ASTASOL® containing 1.000 ± 0.002 g L^{-1} Pt in the form of chloro complex

Table 2 Program decomposition for tunnel dust samples and cleaning patron extractor

Decomposition power	Time (min)	Cleaning power	Time (min)
200 W	2	200 W	2
400 W	2	400 W	2
0 W	5	0 W	2
600 W	10	600 W	5
Cooling	20	Cooling	15

Table 3 The temperature program and measurement conditions applied for ZEEnit 60, Jena

Process	Temperature (°C)	Ramp (°C s^{-1})	Time of retention (s)	Time (s)
Drying	90	5	20	34
Drying	105	3	20	25
Drying	110	2	10	12.5
Pyrolysis	1600	250	10	16
Atomization	2300	1400	8	8.5
Cleaning	2400	500	4	4.2

Other conditions: graphite cuvette within platform, slot width 0.2 nm, used wavelength 265.9 nm, current 8 mA, injection volume 20 µL

in 5% HCl (Analytika, Prague, Czech Republic) was used for measurement of the calibration curve and verification of the method effectiveness. *N*-(α-Carbethoxypentadecyl)-trimethylammonium bromide (Septonex®) was used as a cationic surfactant for SPE treatment of decomposed samples (GNB Inc., Czech Republic). All other used chemicals and reagents were of analytical grade purity.

The hydrophobic Bond Elut C18 sorbent in original columns (500 mg in 3-mL cartridges), particle size 40 µm (Agilent Technologies, HPST s.r.o., Prague, Czech Republic), was used as a stationary phase for preconcentration.

Standard Reference Material of tunnel dust BCR-723 with declared content of Pt metals (Zischka et al. 2002; Sutherland 2007) was analyzed to verify the methods for determination of Pt in environmental samples. This standard was prepared in the same way like the other samples (see the above description). Certified concentration of Pt in the standard preparation was declared in the range of 81.3 ± 2.5 ng g^{-1}.

Results and discussion

Optimization and validation of preconcentration procedure

At first, we focused on optimization and validation of preconcentration procedure, which leads to an increase in concentration of Pt in a sample and simultaneously to removal of ions and compounds potentially masking determination of the analyte. In principle, the Bond Elut C18 is the most hydrophobic bonded silica sorbent for retaining nonpolar compounds in existence. Platinum, in the form of a chloro complex, creates ion associates with a cationic surfactant and this associate exerts high affinity to the octadecyl-modified silica gel sorbent. The sorption procedure described in (Komendová-Vlašánková and Sommer 2002) was optimized with model samples to reach maximal sorption recovery of Pt. We tested a wide range of the following conditions: sorption rate; the type and concentration of association agents; type, pH and volume of eluent mixtures; acidity of sorbed and measured solutions; and various interferences originating from presence of interfering ions, which occurred in digested real samples of soil, plant material and tunnel dust. After ten repeated measurements under the optimal conditions, the recovery rate ranging between 95.2 ± 1.5% was achieved. It was also found that this sorption process is reproducible and robust, which means that it does not depend on type of matrix and Pt concentration. In other words, large excesses (thousand times in comparison with Pt concentration) of either accompanying anions (chlorides, nitrates, nitrites, sulfates) or cations (sodium and potassium ions, calcium and magnesium ions, iron ions, aluminum ions and other heavy metal ions) did not interfere with the determined analyte. Therefore, the preconcentration method was proved to be suitable for determination of Pt in sampled soils, dust and plants in the range of several concentration orders. This method was also validated using the BCR certified reference material; 83.0 ± 3.6 ng g^{-1} Pt was found, which is in a good agreement with a certified reference value of 81.3 ± 2.5 ng g^{-1}.

Determination of Pt in tunnel dust, soils and plant material

Platinum was determined in nine samples of tunnel dust, 12 soil samples and 12 corresponding samples of grass collected at the same place (Table 1). All results are summarized in Fig. 1 which shows that Pt concentrations in tunnels reached their highest levels before cleaning when they ranged from 66.3 to 192 ng g^{-1}. Cleaning of tunnels, which is carried out twice a year, resulted in a significant decrease in Pt levels that oscillated between 29.2 and 38.2 ng g^{-1}. We hypothesize that the concentration of Pt measured after cleaning reflects capability of tunnel dust to accumulate it within a month, which represents sampling time after tunnel cleaning. The concentration found before cleaning reflects capacity of the tunnel to retain Pt particles within 6 months when the tunnels are regularly cleaned. Comparison of averaged values (Fig. 2) implies that accumulation rate decreases in time. We assume that this is caused by progressive

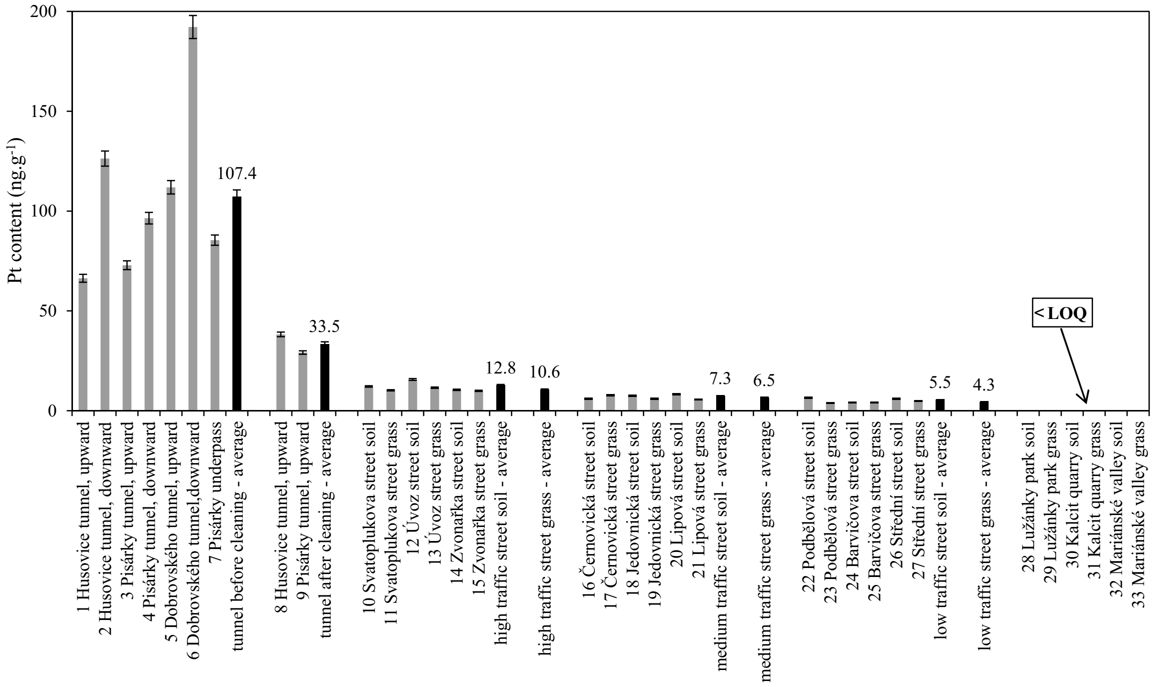

Fig. 1 Platinum concentration in ng g^{-1} determined in tunnel dust, soil, and plant samples

saturation of tunnel dust absorption capacity and by outlet of the dust from the tunnel. This is partially reflected in elevated concentration of Pt in underpass (sample 7).

Platinum concentrations ranged from 10.5 to 15.7 ng g^{-1} in soils and oscillated from 10.0 to 11.6 ng g^{-1} in grass; the soil and grass samples were collected in the vicinity of roads with high car traffic. In the samples collected in the area with medium volume of automobile traffic, Pt contents ranged from 6.02 to 8.44 ng g^{-1} in soil and from 5.61 to 7.85 ng g^{-1} in grass. The area with low car traffic, located mainly in the outskirts of the city, was characterized by lower values ranging from 4.00 to 6.48 ng g^{-1} in soil and from 3.99 to 5.02 ng g^{-1} in grass. As expected, these values are one to two orders lower than those found in tunnel dust, which was caused by better diffusion of emission exhausts into free space and by removal of dust by rain precipitations. Surprisingly, concentration of Pt in soil and grass (dry mass) reached comparable levels, which implies relatively easy transport of Pt from soil to grass. As aforementioned, bioavailability of Pt is determined by its solubility (Pawlak et al. 2014). The finding on comparable concentrations in grass and soils is in contrast to the observation showing that only a low portion of Pt is rapidly (within a vegetation period) solubilized. Nevertheless, the influence of Pt dispersed in air plays also significant role.

Rest and recreational areas of Brno such as parks and valleys showed concentrations of Pt below the quantification limits of the suggested technique; this affirms the assumption that traffic represents the main source of higher concentration of Pt in environmental compartments.

Figure 3 shows average Pt content found in different samples with respect to the frequency of car traffic volume excluding the tunnels. Dependency of Pt concentration on traffic volume indicates that an increase in Pt concentration is not linearly proportional to rise in number of cars; the difference between categories of traffic volume 1 and 20 thousand cars per hour is really minor. We assume that this may be attributed to speed of cars and driving style, but this supposition goes beyond the scope of this paper.

The findings of the authors corroborate with results of other researches who reported data from other cities in Europe and also around the world (Bencs et al. 2011; Dubiella-Jackowska et al. 2009; Hooda et al. 2007; etc.). The obtained results show that the inhabitants of large cities are continuously exposed to emissions of Pt metals. Given the ever-increasing vehicular traffic (Matthey 2017) and irreplaceability of Pt metals in catalysts, the population will be exposed to rising concentrations of these substances. With regard to possible allergenic reactions to Pt compounds, the findings of this study are supposed to contribute to

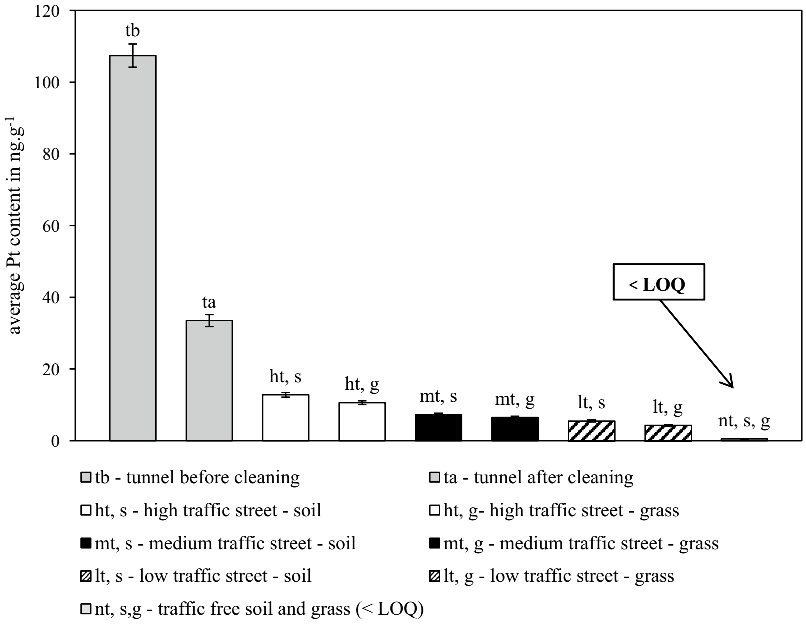

Fig. 2 Representation of the average platinum content in ng g^{-1} in various objects—tunnel dust, soil and grass samples from city of Brno (2015–2016)

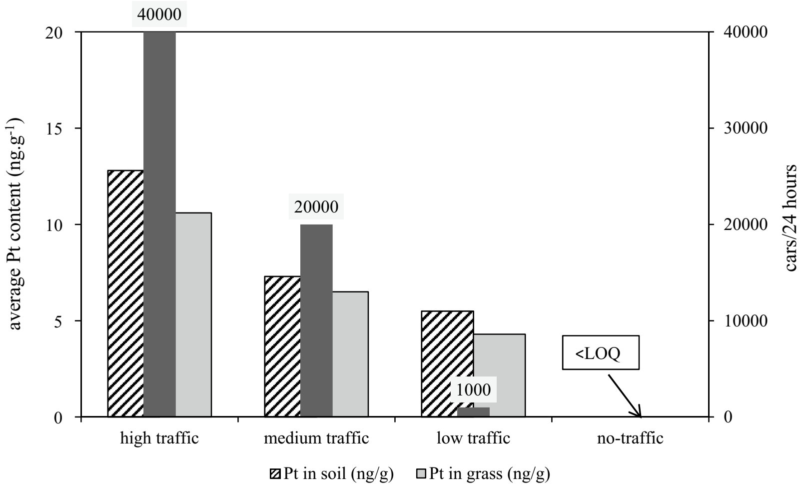

Fig. 3 Dependence of platinum content (ng g^{-1}) on traffic volume

introduction of complete monitoring and determination of Pt effects in such polluted environment.

Conclusion

The results of this study show that the environmental compartments of middle-sized cities exposed to car traffic are contaminated with platinum (Pt). It was demonstrated that the environmental Pt concentrations depend on intensity of automotive traffic. Tunnels represent specific urban sites, where dust containing Pt accumulates. Levels of Pt in tunnels are several times higher than those in soil or grass; after cleaning of tunnels, concentration of Pt is rapidly restored. Compared with Pt levels in tunnels, its lower concentrations in open places are given by conditions for dispersion of dust particles to the atmosphere and also by the effects of weather, especially of rainfall events.

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References

Abdou M, Schäfer J, Cobelo-García A, Neira P, Petit JCJ, Auger D, Chiffoleau JF, Blanc G (2016) Past and present platinum contamination of a major European fluvial-estuarine system: insights from river sediments and estuarine oysters. Mar Chem 185:104–110

Bencs L, Ravindra K, Van Grieken R (2003) Methods for the determination of platinum group elements originating from the abrasion of automotive catalytic converters. Review article. Spectrochim Acta Part B 58:1723–1755

Bencs L, Ravindra K, Van Grieken R (2011) Platinum: environmental pollution and health effects. In: Encyclopaedia of Environmental Health. Elsevier, pp 580–595

Castillo MLA, de Torres AG, Alonso EV, Cordero TS, Pavón JMC (2012) Multi-element determination of Pt, Pd and Ir traces in environmental samples by ICP-MS after pre-concentration. Talanta 99:853–858

Chwastowska J, Skwara W, Sterlińska E, Pszonicki L (2004) Determination of platinum and palladium in environmental samples by graphite furnace atomic absorption spectrometry after separation on dithizone sorbent. Talanta 64:224–229

Dubiella-Jackowska A, Kudłak B, Polkowska Ż, Namieśnik J (2009) Environmental fate of traffic-derived platinum group metals. Crit Rev Anal Chem 39:251–271

Ek KH, Morrison GM, Rauch S (2004) Environmental routes for platinum group elements to biological materials—a review. Sci Total Environ 334–335:21–38

Goncalves A, Domínguez JR, Alvarado J (2008) Determination of Pd, Pt and Rh in vehicles escape fumes by GF-AAS and ICP-OES. Talanta 75:523–527

Hooda PS, Miller A, Edwards AC (2007) The distribution of automobile catalysts-cast platinum, palladium and rhodium in soils adjacent to roads and their uptake by grass. Sci Total Environ 384:384–392

Kan SF, Tanner PA (2004) Determination of platinum in roadside dust samples by dynamic reaction cell-inductively coupled plasma-mass spectrometry. J Anal At Spectrom 19:639–643

Komendova R (2018) The use of bioindicators for assessing atmospheric pollution with platinum metals. Fresenius Environ Bull 5A:3444–3451

Komendová-Vlašánková R, Sommer L (2002) Separation and preconcentration of platinum group metals and gold on modified silica and XAD sorbents in the presence of cationic surfactants for their determination by ICP-AES. Collect Czech Chem Commun 67:454–470

Kononova ON, Melnikov AM, Borisova TV (2012) Simultaneous sorption recovery of platinum and rhodium from sulfate-chloride solutions. Hydrometallurgy 117–117:101–107

Kosárová H, Komendová R, Skeřil R (2015) Development of an analytical method for the determination of platinum in urban dust in the agglomeration of Brno, Czech Republic. Fresenius Environ Bull 6:2070–2075

Leopold K, Maier M, Schuster M (2008) Long-term study of palladium in road tunnel dust and sewage sludge ash. Environ Pollut 156:341–347

Machado RC, Amaral CDB, Schiavo D, Nóbrega JA, Rita A (2017) Complex samples and spectral interferences in ICP-MS: evaluation of tandem mass spectrometry for interference-free determination of cadmium, tin and platinum group elements. Microchem J 130:271–275

Matthey J (2017) The platinum market remains strong as industrial and auto sector increases offset a reduced demand for jewelry. Focus Catal 2017:2

Mihaljevič M, Galušková I, Strnad L, Majer V (2013) Distribution of platinum group elements in urban soils, comparison of historically different large cities Prague and Ostrava, Czech Republic. J Geochem Explor 124:212–217

Moldovan M, Palacios MA, Gómez MM, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Pettersson C, Wass U, Luna M, Saenz JC, Santamaría J (2002) Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. Sci Total Environ 296:199–208

Niemelä M, Perämäki P, Piispanen J, Poikolainen J (2004) Determination of platinum and rhodium in dust and plant samples using microwave-assisted sample digestion and ICP-MS. Anal Chim Acta 521:137–142

Orecchio S, Amorello D (2011) Platinum levels in urban soils from Palermo (Italy); analytical method using voltammetry. Microchem J 99:283–288

Pawlak J, Łodyga-Chruścińska E, Chrustowicz J (2014) Fate of platinum metals in the environment. Review article. J Trace Elem Med Biol 28:247–254

Ravindra K, Bencs L, Van Grieken R (2004) Platinum group elements in the environment and their health risk. Review article. Sci Total Environ 318:1–43

Reith F, Campbell SG, Ball AS, Pring A, Southam G (2014) Platinum in Earth surface environments. Earth Sci Rev 131:1–21

Rosner G, König HP, Coenen-Stass D (1991) Platinum. Environmental health criteria 125. World Health Organization, Geneva

Spaziani F, Angelone M, Coletta A, Salluzzo A, Cremisini C (2008) Determination of Platinum group elements and evaluation of their traffic-related distribution in Italian Urban environments. Anal Lett 41:2658–2683

Sutherland RA (2007) Platinum-group element concentrations in BCR-723: a quantitative review of published analyses. Anal Chim Acta 582:201–207

Vlašánková R, Sommer L (1999) Solid phase extraction and preconcentration for the determination of trace amounts of platinum group metals in environmental and biotic material. A critical Review. Chem Pap 53:200–209

Vlašánková R, Otruba V, Bendl J, Fišera M, Kanický V (1999) Preconcentration of platinum group metals on modified silicagel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates. Talanta 48:839–846

Wang Y, Li X (2012) Health risk of platinum group elements from automobile catalyst. Procedia Eng 45:1004–1009

Wiseman CLS, Zereini F (2009) Airborne particulate matter, platinum group elements and human health: a review of recent evidence. Sci Total Environ 407:2493–2500

Zereini F, Alt F (2000) Anthropogenic platinum—group element emissions. Their impact on man and environment. Springer, Berlin

Zimmermann S, Messerschmidt J, Bohlen A, Sures B (2003) Determination of Pt, Pd and Rh in biological samples by electrothermal atomic absorption spectrometry as compared with adsorptive cathodic stripping voltammetry and total-reflection X-ray fluorescence analysis. Anal Chim Acta 498:93–104

Zischka M, Schramel P, Muntau H, Rehnert A, Gomez MG, Stojanik B, Quevauviller P, Maier EA (2002) A new certified reference material for the quality control of palladium, platinum and rhodium in road dust, BCR-723. Trends Anal Chem 21:851–868

Příloha 7

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THE USE OF BIOINDICATORS FOR ASSESSING ATMOSPHERIC POLLUTION WITH PLATINUM METALS

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ABSTRACT

This work deals with the study and selection of suitable bioindicators for the assessment and detection of environmental contamination by platinum metals. Lichen (*Xanthoria parietina*), moss (*Pleurozium schreberi*) and needle (*Pinus nigra*) were tested as bioindicators. After optimization of the analytical procedures for decomposition, pretreatment, preconcentration and determination of platinum and palladium, platinum metals contamination in areas with high car traffic was determined by the original species technique. The contamination of the environment was determined depending on the distance from the source of pollution and also the sorption capacity of these individual biomaterials was tested. A higher content of platinum metals was found in lichen samples, then in moss and the lowest concentrations were found in the needles. The platinum and palladium concentrations ranged from units to tens in ng.g^{-1} and the high bioavailability of palladium was confirmed. The most appropriate bioindicator was lichen and can be recommended to monitor the content of bioavailable forms of these elements in the environment. There was no confirmation of the massive spread of these pollutants over longer distances, the highest concentration values being found in the immediate vicinity of the road. In particular, the increasing concentrations of these metals have been confirmed in the environment, as well as in biomatrics.

KEYWORDS:
Platinum, palladium, bioindicators, lichen, moss, needles, atmospheric pollution, AAS, solid phase extraction.

INTRODUCTION

The current problem of today is the pollution of the atmosphere and the whole environment with emissions from automobile transport. To date, the most commonly studied pollutants have been toxic fumes emitted by motor vehicles and which are included in the emission limits of EURO standards valid in the territory of the European Union. These pollutants are, in particular, hydrocarbons, nitrogen oxides, carbon monoxide and solid particles. However, it is also important that other substances, potentially toxic, are released into the surrounding atmosphere during the combustion process. Such substances are platinum metals, which form the essential and most important part of automotive catalysts [1, 2]. These platinum metals (especially platinum, palladium and rhodium) catalyze the conversion of toxic gases into non-toxic (hydrocarbons to carbon dioxide and water vapor, carbon monoxide to carbon dioxide, nitrogen oxides to elemental nitrogen) by oxidation-reduction reactions to meet the required EURO Standards. During vehicle travel, the surface of the catalyst is chemically and physically stressed, in particular by alternating oxidation-reduction conditions, high temperature and mechanical abrasion, and the platinum metals are emitted into the environment. Since the introduction of automotive catalytic converters, the content of these metals has continually increased in all environmental compartments [3-5].

There are many methods and studies on the detection of environmental pollution. Most of them, however, face the problem of high cost of implementation and extensive time and spatial sampling. This is why the interest in using bioindicators to detect environmental pollution has increased [6-9].

A bioindicator refers to an organism where environmental pollution is evaluated at a particular site. Sensitive bioindicators are organisms that show specific or nonspecific effects in response to exposure to a particular element, substance or mixture of substances in the environment. These bioindicators are characterized by having a narrow tolerance range and responding to the low stresses of the stressor. Their most common use is in air monitoring, where plants rather than animals are used. Accumulating bioindicators accumulate one or more elements or compounds from the environment. Pollutants are taken out of the environment and accumulated in their bodies without visible damage and the intake is related to the concentration in the surrounding environment. These bioindicators have a very wide range of tolerance. They are particularly valuable in assessing the chemical environmental impacts. The bioindicator must have a number of properties. Among the most important are the measurable response in response to stress, the response to stress reflects the entire ecosystem population response, responds proportionally to degree of pollution or degradation, relatively narrow ecological valency, but adequate local population density, including areas concerned, relatively stable against moderate climatic and environmental variability, tolerate long exposure to the toxicant without death, react in a timely manner to ecosystem change, long-lived organism, seldom or poorly mobile, readily available for easy sampling and appropriate size.

Plant bioindicators are divided into several groups. The first group contains passive and active (exposure) bioindicators and the second group of accumulation and reaction bioindicators. In passive bioindication selective damage to plant parts (reaction indicator) or accumulation of some substances in selected plants (accumulation bioindicator) is used. In this type of bioindication, either crops or plants growing in the interest area are used. The active (exposure) bioindication is based on the fact that the selected plants are exposed to environmental influences, which subsequently react with the accumulation of the monitored substances (storage indicator) or damage (the reaction indicator).

Lichens are the double organisms (fungus-algae or cyanobacteria) used for bioindication of air pollution loads, such as sensitive and accumulation indicators. In connection fungi and algae, and algae represents the portion of the plant that ensures the production of nutrients it contains chlorophyll, whereas sponge ensures intake of water and minerals. Lichens are considered to be the slowest growing organisms, although they grow almost year round. On the other hand, lichens are of very high age. Lichens are among the most valuable bioindicators of air pollution. Their surface is not covered by a cuticle or other protective element, which is one of the facts why they are able to sorb over the entire surface of their plant body. Lichens can accumulate elements up to a level exceeding their capacity, which is used for their use as indicators of air pollution by trace elements around the world. Such bioindicators have proved to be a simple and cost-less method that provides results that can be based on predictions of potential dangers for the human organism.

Mosses are green but not vascular plants of small growth, for which the ability to hold water is typical. They occur in damp and shady places. They have a rather complicated structure. Water absorbs the entire surface of the insole and spreads it through conductive meshes or the easily wetting surface of the plants. When a waxy cuticle is developed, it can serve to direct the flow of water to certain parts of the mossy plant. The way moss manages the water allows them to use even very small and horizontal precipitation. The large surface and easy penetration of the insole also means that mosses are sensitive to air quality and precipitation. Moss as bioindicator is the most popular of all bioindicators. This is because moss does not have technical or analytical problems in determining environmental pollution than in lichens or bark.

Mosses have many other benefits. They are geographically extensive, growing in different environmental conditions in both industrial and urban agglomerations. Additionally, the mosses do not have overhead organs covered by a cuticle, so metal ions easily penetrate into the cell wall. Since they do not have true roots, all income is only from the atmosphere. The main source of the substances is atmospheric deposition, the dissolution of which is caused by atmospheric precipitation, regular wet morning wetting and acidic pectin substances secretion. Due to the high wettability and the large surface of the cell walls, the mosses have a high sorption capacity. For many, these elements increase by binding to polygalacturonic acid, pectins, and proteins in the cell wall membranes.

Needles also showed appropriate plant bioindicators, mainly due to the intake of pollutants by their waxy layer. The needle surface consists of a thick cuticle with a cuticular wax. Most needles also have very stiff skin with different protective layers. These adaptations significantly reduce the evaporation of water, which is very important in the winter when the intake of water from the frozen soil is prevented. Pine black is suitable for long-term and annual exposure. Exposed pine trees cut off one-year needles.

In general, biomonitoring of metals according to the used bioindication technique can be divided into transplantation techniques (in the transplant procedure, the bioindicators are transplanted from the unpolluted area to the site of the contamination), bag techniques (the clean biomaterial is put into the bags and exposed for some time to the exposure in the contaminated area) and techniques of native species. In this work the technique of bioindication using the original species was used. This technique is the easiest and most convenient and is based only on the sampling of bioindicators from their original site and the determination of the elements or compounds it contains [10]. The aim of this study was to evaluate the possibility of using bioindicators for evaluation of environmental pollution by selected platinum metals.

MATERIALS AND METHODS

Instruments and equipment. All measurements of real samples and optimization of the method were performed on the atomic absorption spectrometer with electro thermic atomization ZEEnit 60 (AnalytikJena AG, Germany) with Zeeman background correction. This device is equipped with an auto sampler and WinAAS Software. A hollow cathode lamp for platinum (P840, Photron, Australia) and palladium (3UNX Pd, Heraeus, England) was used as the source of primary radiation, and a graphite cuvette with a platform was used for all measurements.

A sorption apparatus was used to preconcentration the sample, which consisted of peristaltic pump (PCD, 82.4 K) with four cassettes (ISMATEC ISO 649) by which samples were drawn through a silicone tubing directly into Agilent's Bond Elut-C18 solid phase extraction columns. These columns were attached to the vacuum system (Baker J.T., spe-12G), which was connected to a water pump.

To determine the sorption capacity of each bioindicator the Heidolph VIBRAMAX 110 shaker was used in which the samples were shaken in plastic samplers.

Chemicals. The platinum and palladium standards were used to optimize the method. These were certified reference standard materials - aqueous calibration solutions with concentration of 1 ± 0,002 g.dm^{-3} in 5% HCl, from the Czech Metrology Institute, ASTASOL® Analytika s.r.o., Czech Republic.

Hydrochloric acid 37% (HCl), Analytika s.r.o., Czech Republic. Nitric acid 67% (HNO_3), ethyl alcohol absolute p.a. (CH_3CH_2OH), acetonitrile (CH_3CN), all Penta, Czech Republic.

Septonex® carbethoxypentadecyltrimethylammonium bromide ($C_{21}H_{44}O_2NBr$), GNB a.s., Czech Republic.

Silica gel C18, Agilent Technologies, Lake Forest, California, USA. The column with volume 3 cm^3 contains 500 mg of sorbent (particle size 47-60 μm).

Characteristic of samples. The original species were used in this work for two different experiments. In the first experiment (analysis A), the original bioindicators were used to determine the ability and rate of bioindicators to adsorb the platinum metals. From the bioindicators, the species of moss (*Pleurozium schreberi*), lichen *Flavoparmelia caperata* and black pine needles (*Pinus nigra*) were used. There unpolluted samples of moss, lichen and needles were taken in the Šumava National Park, Czech Republic.

To determine the rate of platinum sorption, the sorbed amount (Qad) of platinum or palladium was calculated per unit weight of the sorbent according to the formula

$$Q_{ad} = \frac{(C_i - C_e) \cdot V}{m}$$

C_i and C_e represent the input concentration and the concentration after sorption in μg.dm^{-3}, V is the volume of the solution in dm^{-3} and m is the sorbent mass in grams (g) [11].

In the second experiment (analysis B) the current environmental pollution was assessed. For this purpose, five sites of assumed platinum pollution were selected in the city of Brno (Czech Republic) and one site where it was not supposed contamination of platinum metals. This was selected for comparison with contaminated samples. Polluted samples were taken in close proximity to traffic roads. Locations in the city of Brno were selected according to the national census of roads and motorways in the city of Brno. All the selected roads were first class roads with a frequency of automotive transport of tens of thousands of cars per day. The sampling points are shown in Table 1. A sample of moss, lichen and needle was collected at each site. For the determination of platinum metal pollution in the city

TABLE 1
Characterization of real samples

No. of sample	Sample identification	Place of sampling	GPS	Description of sampling condition
	Analysis A			
1.	A/1 – moss	Šumava National Park	48.936494452, 13.813060024	1300 m from the 3rd class road, in the forest
2.	A/2 – lichen			
3.	A/3 - needles			
	Analysis B			
4.	B1/1 – moss	Horní Lažany	49.103797459, 15.795807838	300 m from the 3rd class road, without pollution
5.	B1/2 – lichen			
6.	B1/3 - needles			
7.	B2/1 – moss	Tomkovo Square	49.213903779, 16.635720134	15 m from the 1st road
8.	B2/2 – lichen			
9.	B2/3 - needles			
10.	B3/1 – moss	Hradecká Street	49.223448395, 16.58082068	20 m from the 1st road
11.	B3/2 – lichen			
12.	B3/3 - needles			
13.	B4/1 – moss	Úvoz Street	49.20173908, 16.592595577	10 m from the 1st road
14.	B4/2 – lichen			
15.	B4/3 - needles			
16.	B5/1 – moss	Halasovo Square	49.22452748, 16.620748043	10 m from the 1st road
17.	B5/2 – lichen			
18.	B5/3 - needles			
19.	B6/1 – moss	Opuštěná Street	49.185507813, 16.613076925	10 m from the 1st road
20.	B6/2 – lichen			
21.	B6/3 - needles			

of Brno, the same species of the moss (*Pleurozium schreberi*), the lichen (*Xanthoria parietina*) and the needles (*Pinus nigra*) were selected. A set of samples with zero platinum and palladium-based pollutants (Horní Lažany, Vysočina Region) were sampled at a location 300 meters away from the 3rd class road.

The sampling sites were chosen so that the moss, the lichen and pine needles of selected species were always located in the same place. Therefore the selection of these localities was considerably limited in the territory of the city of Brno. During sampling, the attempt was made to preserve the structure of the bioindicators, or to minimize damage to it.

Decomposition and pretreatment of real samples. To verify the bioindicator sorption capability, the original unpolluted samples for analysis were used. The samples were first allowed to dry at room temperature for 3 weeks. Subsequent unwanted materials were removed (soil, leaves, grass, bark ...) and the samples were weighed into polypropylene samplers. The weight of the samples ranged from about 1.5 g for the moss, about 1 g for the lichen and about 2 g for the needles. About 25 cm^3 of the solution containing the platinum and palladium amounts was added to the sample thus weighed. After addition, the flask was capped and the sample was shaken in shaker for 20 minutes. Subsequently, the sample was filtered through glass fiber filter into volumetric flasks and measured on an ET-AAS instrument. In this experiment (A) the sorptive capacity for five concentrations of Pt and Pd (300, 450, 1000, 1300 and 1500 μg.dm^{-3}) was studied. For each concentration, 3 samples of the bioindicator were analyzed, which were measured 5 times on the ET-AAS instrument so that the final solution concentration after sorption was a mean of 15 values. In addition, solutions of Pt and Pd were prepared at each concentration both in acidic medium (0.1 mol.dm^{-3} HCl) and in distilled water.

Firstly (for analysis B), the samples were dried at room temperature for 3 weeks. After drying, undesirable materials have been removed. Samples were weighed into the Erlenmeyer flask on analytical scales. The weight of the sample ranged from 2.5 to 3 g. For the decomposition of samples, a 1:3 mixture of nitric acid and hydrochloric acid was used. At first, 15 cm^3 of nitric acid was added to the samples and Erlenmeyer flask was covered with a clock glass. Thus the samples were left for 24 hours. Subsequently, the flask was stirred and 45 cm^3 of hydrochloric acid was added and the samples were boiled under reflux for 2 hours. Then, 25 cm^3 of distilled water was added to the mixture and the mixture was refluxed for another 15 minutes. Then filtration with glass fiber filter was carried out and the mixture was transferred to a volumetric flask. Subsequently sorption and preconcentration by the SPE method were performed. The column conditioning was first done. Before sampling, 5 cm^3 of 0.005 mol.dm^{-3} of Septonex® were added to the sample. Then the sample was applied. After sorption, the sorbent was washed and finally eluted the analyte. The eluate was evaporated in Teflon plates on an electric heating plate almost to dryness and then transferred to a 10 cm^3 volumetric flask by 0.1 mol.dm^{-3} HCl. The platinum and palladium concentrations were measured with ET-AAS in thus pretreatment sample.

RESULTS AND DISCUSSION

Measurement conditions. Determination of platinum was carried out at a selected wavelength of 265.9 nm and palladium at a wavelength of 247.6 nm. The temperature program was very similar for both of these metals, the only difference was when atomizing at the time of stay, when the platinum has an optimum residence time of 8 seconds and a palladium of 6 seconds. The cuvette with platform was used for all measurements. The width of the slot was 0.2 nm, the used current 8 mA, and the volume of the dose sample 20 μl.

TABLE 2
Temperature program for Pt and Pd

Step	Temperature (°C)	Temperature rise (°C/s)	Residence time (s)
Drying 1.	90	5	20
Drying 2.	105	3	20
Drying 3.	110	2	10
Pyrolysis	950	250	10
Atomization	2200	1400	6 (Pd), 8 (Pt)
Cleaning	2400	500	4

The calibration curve was obtained by measuring 10 solutions of the selected concentration range. The individual calibration functions were chosen to include platinum and palladium concentrations present in real samples. The detection limit (LOD) and the limit of determination (LOQ) were determined from this calibration curve. The limit of detection for platinum was 2.627 μg.dm^{-3} and limit of quantification 8.758 μg.dm^{-3}. For palladium the LOD was obtained 2.282 μg.dm^{-3} and LOQ 7.605 μg.dm^{-3}.

Preconcentration procedure. To verify the efficiency simultaneously sorption of platinum [12] newly with palladium (for analysis B), a model procedure was performed to confirm the sorption and concentration of platinum and palladium in one step. The 200 cm^3 volumetric flask containing the platinum and palladium standard, 0.005 mol.dm^{-3} Septonex®, was added to the mark with 0.1 mol.dm^{-3} HCl. Prior to sorption, column conditioning was carried out, using 10 cm^3 of ethanol, 10 cm^3 of distilled water, and finally 10 cm^3 of 0.005 mol.dm^{-3} Septonex®. After conditioning, 50 cm^3 of the sample was applied, and the sample was absorbed and concentrated, and then the sample was eluted with 10 cm^3 of acetonitrile. The eluate was evaporated in teflon plates with the help of a heating plate almost to dryness, then 10 cm^3 of 0.1 mol.dm^{-3} HCl was added. Such concentrated samples were measured on an ET-AAS instrument.

First, the ET-AAS sample was measured before sorption. Subsequently, 10 samples after sorption were measured to determine the efficiency of sorption and repeatability. From the calibration curve, sample concentrations were calculated. The average return on these 10 samples was 101.5±1.2 % for platinum and 100.2±1.4 % for palladium. Thus, the effective preconcentration of platinum and palladium was confirmed in one step using the same sorption procedure. There will be an acceleration of all analyzes and a significant reduction in the cost of one analysis.

Sorption ability of selected bioindicators (analysis A). It has been assumed that lichen will exhibit the best sorptive capacity of selected bioindicators. Its high sorption capability is due to the fact that it is not covered by a cuticle or other protective element and is capable of sorbing with its entire surface. In addition, lichens are able to accumulate elements up to a level exceeding their capacity. It was further assumed that relatively less than lichen would have moss sorption abilities. Mosses are very extensive, making them very popular bioindicators. Although their above-ground organs are also not covered by cuticle, they are not able to exceed their sorption capacity despite their high sorptive capacity. The least suitable for the bioindication of platinum metals should probably be the needles because the surface is a strong cuticle with a cuticular wax, so the sorption rate is limited by this cuticle and is more suitable for determining organic contamination.

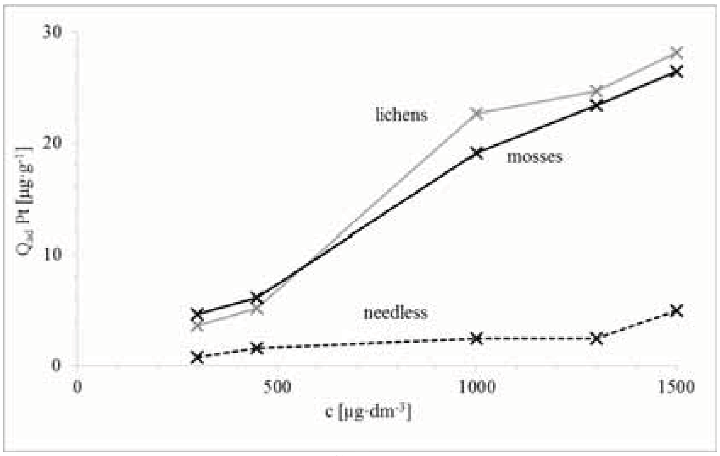

FIGURE 1
The comparison of sorption capacity Q_{ad} for various bioindicators for Pt

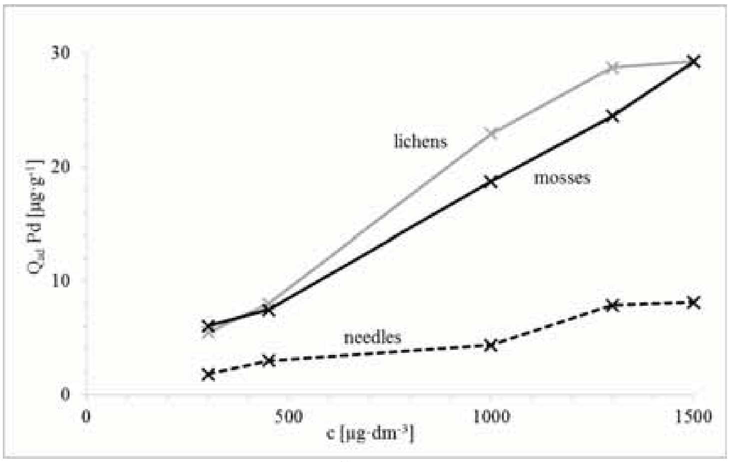

FIGURE 2
The comparison of sorption capacity Q_{ad} for various bioindicators for Pd

Therefore, a comparison of the sorption of both platinum metals was made in the selected "pure" bioindicators from non-contaminated area (see Table 1). It is evident from Figure 1 and Figure 2 that the initial assumptions were confirmed and the lichen was evaluated as the best sorbing bioindicator, followed by mosses and the least platinum metals captured the needles. The experiments were carried out in the absence and presence of 0.1 mol.dm^{-3} hydrochloric acid. Sorption in acidic medium was chosen because the platinum metals in very low concentrations are easily sorbed on the walls of glassware. To prevent this sorption, it is necessary to acidify the solution. In this case, more efficient sorption occurs in all cases in more acidic medium. This is related to the mobility and bioavailability of platinum metals at lower pH values.

It was confirmed that the best bioindicator capable of sorption of platinum and palladium is lichen, in particular *Xanthoria parietina*. The moss *Pleurozium schreberi* does not achieve such sorption rates as lichen. The needles *Pinus nigra* markedly less captured both platinum metals. It can be argued that the most suitable bioindicator, which was tested for the assessment of environmental pollution by platinum metals, is lichen and the least suitable are needles.

Platinum metals are in the atmosphere at very low concentrations. Specifically for the city of Brno in the urban area the concentration of platinum is in range 2.3-51.5 pg.m^{-3} [12]. It has been verified that all the platinum metals present in the atmosphere are capable of absorbing all three bioindicators due to their sorption abilities.

Current environmental pollution (analysis B). The selected bioindicators were tested to determine the actual pollution in selected localities in the city of Brno. In the case of moss, the lowest sorbed amount of palladium in Horní Lažany was measured. The original types of bioindicators from Horní Lažany were analyzed for comparison with the polluted species from localities in Brno, where it was assumed that would be "pure" bioindicators. The highest sorbed amount of palladium on moss, thus the most polluted palladium site with bioindication by moss, was measured in Opuštěná Street. The values of the sorbed amount of palladium in mosses in other localities are not particularly different from the highest measured value. All measured values of the sorbed amount of platinum metals in selected localities of Brno are shown in Table 3.

Absorbed quantities of palladium on the needles were comparable to those measured in moss and very low compared to lichen. The lowest value of palladium was measured again in the presumed "clean" localities Horní Lažany. The highest value of palladium for bioindication of needles was measured in Hradecká Street. This value significantly exceeds the measured values of other localities, and the bioindication of the needles was the most contaminated locality by palladium.

Lichen adsorbs the most palladium unambiguously. The lowest sorbed amount of palladium was measured in Horní Lažany. The highest and also the most contaminated locality of palladium in the lichen bioindication was the Úvoz site. At Halas Square, Opuštěná Street and Tomkovo Square, comparable values were measured.

For moss, the highest sorbed amount of platinum was measured on Hradecká Street. This value clearly exceeds all other values. Tomkovo Square, Halasovo Square and Úvoz are similar in terms of polluting platinum. The lowest value was measured in Horní Lažany. All the measured values at this location were below the detection limit. A slightly higher value than in the "clean" moss was measured on Opuštěná Street. All measured platinum content values are listed in Table 3.

TABLE 3
Palladium and platinum contaminations in selected bioindicators

No. of sample	Location	Sample identification	Palladium content (ng.g^{-1})	Platinum content (ng.g^{-1})
4.	Horní Lažany	B1/1 moss	2.979	<LOD
5.		B1/2 lichen	5.140	<LOD
6.		B1/3 needles	3.017	<LOD
7.	Tomkovo Square	B2/1 moss	6.985	14.18
8.		B2/2 lichen	27.37	4.223
9.		B2/3 needles	8.147	7.278
10.	Hradecká Street	B3/1 moss	7.432	59.40
11.		B3/2 lichen	14.23	14.88
12.		B3/3 needles	12.09	<LOD
13.	Úvoz Street	B4/1 moss	7.224	11.41
14.		B4/2 lichen	47.08	12.54
15.		B4/3 needles	5.682	<LOD
16.	Halasovo Square	B5/1 moss	7.124	16.98
17.		B5/2 lichen	22.89	23.18
18.		B5/3 needles	6.740	3.805
19.	Opuštěná Street	B6/1 moss	8.449	<LOD
20.		B6/2 lichen	23.98	5.645
21		B6/3 needles	7.057	4.950

Absorbed amount of platinum on the needles was lowest compared to moss and lichen. The lowest value was measured in Horní Lažany. On the contrary, the highest value was measured at Tomkovo Square. In Hradecká Street and Úvoz were slightly higher values than in "pure" needles. At Halasovo Square and Opuštěná Street, the pollution rate was relatively the same.

The lichen sorbed the most platinum of all three bioindicators. The lowest rate of platinum sorption was again measured by lichen in bioindication in Horní Lažany and the highest in Halasovo Square. Highest measured value clearly exceeds all others. Street Hradecká along with Úvoz are slightly worse in terms of measured sorbed quantity and Opuštěná and Tomkovo Square have measured slightly higher values than in the "clear" lichen.

Comparison of biomarkers with respect to sorption of platinum is not so clear that which bioindicator has the best sorption capacity. At each site, the sorbed amount of platinum was different for each bioindicator. Therefore, it is not possible to say on which site the largest polluted platinum was found, which would be correspond to all three bioindicators. The lowest contamination was again measured in "clean" bioindicator.

CONCLUSION

In urban agglomerations with busy roads, there are high emissions of platinum metals. This is mainly due to the fact that it cannot be driven smoothly by car or other means of transport, but a "start-stop" drive is needed in which there is an increase in emissions. These emissions are then exposed not only to the environment but also to the population living in the urban agglomerations.

In this work the efficiency of sorption of both platinum and palladium was verified by the SPE method on sorbent modified silica gel. When validating the sorption efficiency, it was confirmed that the optimized conditions for platinum and palladium sorption of the SPE method required 100% efficiencies. This fact has led to the conclusion that platinum and palladium sorption has greatly accelerated and simplified the sorption of both elements simultaneously in one analytical step.

The ability of sorption of platinum metals in moss *Pleurozium schreberi*, *Pinus nigra* needles and lichen *Flavoparmelia caperata* were examined in laboratory conditions. During examining the platinum and palladium sorptivity, it was confirmed that all three bioindicators are capable of platinum and palladium in a wide range of concentrations. The highest sorption capabilities for platinum and palladium were found for lichen and a little less for moss. The smallest sorption skills showed the needles. Since the concentration of platinum metals in the atmosphere is at very low concentrations, it has been confirmed that all of this amount in the air can be fully adsorbed on these bioindicators.

The environmental pollution with platinum metals was investigated in selected localities of the city of Brno (Czech Republic) using the technique of the original species with analyzing collected bioindicators of Schreber's moss (*Pleurozium schreberi*), lichen *Xanthoria parietina* and needles *Pinus nigra*. It was best absorbed palladium by lichen, the needles with moss sorbed palladium similarly. For platinum, it cannot be claimed that some bioindicator is better than others. Values are very different in this measurement. It has been confirmed that the sorption of palladium and platinum for bioindicators is dependent on a number of factors (age, species, weather conditions ...). The results obtained showed that moss was better sorbed platinum in 4 localities out of 6, needles clearly better absorbed palladium in all localities than platinum and lichen, as well as needles, better sorbed palladium in 4 localities of 6.

Higher levels of palladium in lichen are measured by its bioavailability, which increases in the order of platinum metals Pd > Pt ≥ Rh and correspond to other studies [13]. Bioavailability is closely related to the solubility and mobility of the element. Palladium has the best potential for transformation into more soluble, bioavailable compounds after its entry into the environment. On the other hand, platinum, which is less bioavailable, is deposited on the surface of the biosorbent rather than accumulated in the internal structure of the biosorbent. The results of the sorbed amount of platinum are therefore greatly influenced by the weather conditions and atmospheric precipitations to which the biosorbent is exposed. It has been confirmed that the most soluble and mobile in the environment and with the greatest potential to be absorbed into the organism is palladium.

However, it is clear from the findings that the amount of platinum and palladium in the air from automobile transport goes into the environment and all its components. Especially dangerous is their entry into the biota, or to the organisms living in these polluted areas, including the human population.

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REFERENCES

[1] Zereini, F., Alt, F. (1999) Anthropogenic Platinum – Group Element Emissions. Their Impact on Man and Environment. Springer-Verlag. Berlin Heidelberg.

[2] Zereini, F., Alt, F. (2006) Palladium Emissions in the Environment. Analytical Methods, Environmental Assessment and Health Effects. Springer. Berlin Heidelberg New York.

[3] Pawlak, J., Łodyga-Chruścińska, E., Chrustowicz, J. (2014) Fate of platinum in the environment. Journal of Trace Elements in Medicine and Biology. 28, 247-254.

[4] Wang, Y., Li, X. (2012) Health Risk of Platinum Group Elements from Automobile Catalysts. Procedia Engineering. 45, 1004-1009.

[5] Reith, F., Campbell, S.G., Ball, A.S., Pring, A., Southem, G. (2014) Platinum in Earth surface environments. Earth-Science Reviews. 131, 1-21.

[6] Szczepaniak, K., Biziuk, M. (2003) Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution. Environmental Research. 93, 221-230.

[7] Sujetovienė, G., Galinytė, V. (2016) Effects of the urban environmental conditions on the physiology of lichen and moss. Atmospheric Pollution Research. 7, 611-618.

[8] Komendova, R., Nevrla, J., Kuta, J., Sommer, L. (2016) Innovative preconcentration technique on polymer sorbent for simultaneous determination of platinum group metals in the waters and lichen *Hypogymnia Physodes*. Fresen. Environ. Bull. 25, 5172-5179.

[9] Suchara, I., Sucharova, J., Hola, M., Reimann, C., Boyd, R., Filzmoser, P., Englmaier, P. (2011) The performance of moss, grass, and 1- and 2-year old spruce needles as bioindicators of contamination: A comparative study at the scale of the Czech Republic. Science of The Total Environment. 409, 2281-2297.

[10] Forbes, P.B.C., van der Wat, L., Kroukamp, E.M. (2015) Chapter 3 – Biomonitors. Comprehensive Analytical Chemistry. 70, 53-108.

[11] Gupta, B.S., Curran, M., Hasan, S., Ghost, T.K. (2009) Adsorption characteristics of Cu and Ni on Irish peat moss. Journal of Environmental Management. 90, 954-960.

[12] Kosarová, H., Komendová, R., Skeřil, R. (2015) Development of an analytical method for the determination of platinum in urban dust in the agglomeration of Brno, Czech Republic. Fresen. Environ. Bull. 24, 2070-2075.

[13] Colombo, C., Monheimius, A.J., Plant, J.A. (2008) The estimation of the bioavailabilities of platinum, palladium and rhodium in vehicle exhaust catalysts and road dusts using a physiologically based extraction test. Science of The Total Environment. 389, 46-51.

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Příloha 8

KOMENDOVA, R.[*], NEVRLA J., KUTA J. a SOMMER L.
INNOVATIVE PRECONCENTRATION TECHNIQUE ON POLYMER SORBENT FOR SIMULTANEOUS DETERMINATION OF PLATINUM GROUP METALS IN THE WATERS AND LICHEN HYPOGYMNIA PHYSODES.
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INNOVATIVE PRECONCENTRATION TECHNIQUE ON POLYMER SORBENT FOR SIMULTANEOUS DETERMINATION OF PLATINUM GROUP METALS IN THE WATERS AND LICHEN *HYPOGYMNIA PHYSODES*

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ABSTRACT

This study is focused on optimization of preconcentration procedure of trace amounts of platinum group metals (PGMs) by solid phase extraction. Amberlite polystyrene-divinylbezene based sorbent was used for this purpose. Under the optimizing process were optimize number of parameters such as pH value of sorption; type and concentration of complexing agent; concentration and type of cationic surfactant; type, pH, and volume of eluent mixture; acidity of final solution and various interfering influences (presence of various ions, matrix effects). Ammonium-pyrrolidindithiocarbamate, thiourea, 4-(2-pyridylazo) resorcinol and 8-hydroxyquinoline-5-sulfonic acid were used as complexing agents for PGMs. Sorbent was conditioned using cationic surfactant solution. Benzyldimethyltetradecyl ammonium chloride, N-(α-carbethoxypentadecyl)-trimethyl ammonium bromide and benzyldimethyldodecyl ammonium bromide were tested. Mixture of acetonitrile and HCl was proved as eluent. The influences of various concentrations of hydrochloric acid during the complexation, elution and partial evaporation of the eluent prior the determination were tested. Effects of various elements and ions were studied during the sorption and retention on the above mentioned sorbent. Simultaneous determination of PGMs was performed by ICP-MS spectrometer using helium collision cell and internal standard. Detection limits for individual elements at discussed conditions were evaluated. The optimized method of solid phase extraction was applied to spiked real water samples and lichens for testing influences of matrix and efficient of sorption process. It was discovered that recovery ratio of sorption process is diverse for individual studied elements. Acceptable results was achieved for Platinum and Palladium which showed recovery ratio about 100 % and 95 % for Osmium.

KEYWORDS:
Platinum group metals, preconcentration, separation, cationic surfactant, lichens, ICP-MS

INTRODUCTION

The problems of determination of platinum group metals in environmental samples is very topical because of the concentration of PGMs in the environment currently constantly increasing as a result of increasing intensity of car transport. Especially, monitoring of platinum, rhodium and palladium is important because these metals are widely used as catalysts in many branches of industry and primarily as catalytic converters in cars [1]. In this way, the platinum metals get into all environmental media, such as air, airborne dust, water, soil and biological materials [2]. Elevated levels of platinum group metals in these samples were detected only near the busy roads, but also in remote areas with no car traffic [3-5].

Moreover, the use of a number of platinum (II) complexes in medicine against various kinds of cancer has to be mentioned [1, 6-8].

However, the concentrations of these elements in the environment are still very low and they are difficult to detect even using modern analytical methods such as atomic absorption spectrometry with electrothermal atomization (ET-AAS), atomic emission spectrometry with inductively coupled plasma (ICP-OES) or mass spectrometry with inductively coupled plasma (ICP-MS) [9].

The point of analytical determination of PGMs in samples originating from the environment lies mainly on enrichment and removal of interfering influences of matrix. For this purposes, preconcentration and separation process of trace elements prior to the analysis is necessary. Solid phase extraction (SPE) is currently one of the most widely used and effective method of pre-analytical preparation of environmental samples [10, 11]. Low time and financial demands, regeneration of sorbent, low consumption of organic solvents including lower production of waste, achieving of high preconcentration factor and removal of a large number of matrix belong between the major advantages of this method.

This paper is focused on optimizing of preconcentration procedure of PGMs using modified sorbent Amberlite XAD (Strata SDB-L, Phenomenex) and their determination by ICP-MS. Optimized preconcentration procedure was applied to real water samples and lichens.

MATERIALS AND METHODS

Instrumentation. An ICP-MS spectrometer Agilent 7500ce (Tokyo, Japan) equipped with concentric silica nebulizer MicroMist with a double pass Scott-type spray chamber (cooled at +2 °C) was used for analysis. The ICP-MS spectrometer contains an octapole collision-reaction cell, quadrupole analyser and electron multiplier detector which worked in pulse/analogous mode. Other conditions and setting parameters of measurement (ICP-MS) are mentioned in Table 1. The tuning solutions were adjusted to achieve optimal signal stability, low background and low signal of double charged ions, in normal mode. The ion lenses of the spectrometer were optimized prior to each analysis. Polyatomic interferences from the matrix of samples were removed using the octapole collision cell in the helium mode. For monitoring of matrix influence was used internal standard solution which contained mixture of In, Re and Bi in 1% HCl. The instrumental limits of detection (LOD) were based on the 3σ definition [12] and were evaluated from 10 measurements of the blank solutions. These LOD values (in µg L^{-1}) were observed for Ru-0.0184, Rh-0.0025, Pd-0.1177, Os-0.0387, Ir-0.0092 and Pt-0.0084.

Reagent and solutions. A multi element standard stock solution contained 100 ± 0.002 mg L^{-1} platinum group metals in the form of chlorocomplexes in 15% HCl (Analytika, Prague, Czech Republic).

The tuning solutions for ICP-MS contains 1 µg L^{-1} of Ce^{3+}, Li^{+}, Y^{3+} and Tl^{+} in 2% HNO_3 originated by Agilent, HPST s.r.o., Prague, Czech Republic.

TABLE 1
Setting parameters on ICP-MS.

Parameter	Value
Acquisition parameters	
Analytes	^{99}Ru, ^{101}Ru, ^{103}Rh, ^{105}Pd, ^{188}Os, ^{189}Os, ^{191}Ir, ^{193}Ir, ^{194}Pt, ^{195}Pt
Internal standards	^{115}In, ^{185}Re, ^{209}Bi
Integration times	0.5 s (analytes), 0.3 (ISTD 5x repetition/sample)
Sample introduction	
Nebulizer	MicroMist
Spray chamber	Scott double pass
Temperature in spray chamber	2 °C
Sample intake	0.4 mL min^{-1} (sample), 0.125 mL min^{-1} (internal standards)
Inductively coupled plasma	
RF power	1500 W
Plasma gas (Ar)	15 L min^{-1}
Sampling depth	8 mm
Carrier gas	0.75 mL min^{-1}
Make up gas	0.25 mL min^{-1}
Ion optics	
Extract 1	Typically 1 - 4 V
Extract 2	Typically (-130) – (-180) V
Omega bias-ce	Typically (-16) – (-30) V
Omega lens-ce	Typically 1 - 3 V
Collision cell	
Cell entrance	-30 V
Cell exit	-50 V
OctP RF	200 V
OctP Bias	-19 V
Collision gas flow (He)	5.5 mL min^{-1}
Quadrupole	
QP focus	-10 V
QP Bias	-15 V

Solutions of internal standard (100 µg L^{-1} ^{115}In, ^{185}Re and ^{209}Bi in 1% HCl) were prepared from standard solution 1 mg L^{-1} (Analytika, Prague, Czech Republic) by dilution.

Acidity of all solutions was adjusted by anal pure HCl (Analytika, Prague, Czech Republic).

Solutions of cationic surfactants and complexing agents were prepared by weigh out and dissolving of accurate amount in deionized water. N-(α-carbethoxypentadecyl) trimethylammonium bromide $C_{21}H_{44}O_2NBr$ (Septonex®) (GNB a.s., Czech Republic), benzyldimethyltetradecylammonium chloride $C_{23}H_{42}NCl$ (Zephyramine®) and benzyldimethyl-dodecylammonium bromide $C_{21}H_{38}NBr$ (Ajatin®) (both Sigma Aldrich, Steinheim, Germany) were tested as cationic surfactants. Ammonium-pyrrolidindithiocarbamate (APDC), thiourea (TU), 4-(2-pyridylazo) resorcinol (PAR) and 8-hydroxyquinoline-5-sulfonic acid (8-HQS) (all Sigma Aldrich, Steinheim, Germany) were used as complexing agents for PGMs.

The other used chemicals and solvents were all of analytical grade purity.

Modified sorbent Strata SDB-L in original columns (500 mg per 3 mL of column volume) by Phenomenex, Torrance, California, USA, has particle size 55 µm.

Environmental samples. River and peat bog water samples and lichens (class *Hypogymnia physodes*) were collected in Šumava National Park, Czech Republic. Water samples were filtered through the membrane filter Pragopor 6 (Pragochema s.r.o., Czech Republic) with pore size 0.40 µm, prior to the analysis.

Samples of lichens were dried, grinded and decomposed by microwave assisted digestion in presence of *aqua regia* (HCl:HNO_3 3:1). Conditions of microwave digestion in Milestone Digestion/drying mls 1200 (Milestone) equipped with six Teflon™cartridges consisted of five steps were 200W for 2 min, 400 W for 2 min, 0 W for 5 min and 600 W for 10 min. Finally, it was set to 20 min cooling. After digestion and cooling the residue was filtered with the paper filter No. 0.025, collected in a volumetric flask and made up to 50 mL.

SPE arrangement. During sorption process solution was simultaneously pumped through repeatedly used plastic cartridge columns placed in a water-pump-operated vacuum solid phase extraction column processor Baker SPE-12G (J.T. Baker).

A peristaltic pump PCD 82.4 K (Kouřil, Kyjov, Czech Republic) was equipped with four positions for 3 mm silicone tubing to connect the cartridges and operated with an optimized solution flow rate of 1 mL min^{-1}.

An electric hot plate (Altec s.r.o., Czech Republic) served for evaporation of the eluate with organic solvent before ICP-MS determination.

Sorption and elution procedures on Amberlite™ Strata SDB-L. Cartridges with the sorbents were first washed with 10 mL of 96% ethanol and then conditioned with 10 mL of cationic surfactant solution or complexation agent with selected concentration. Optimization studies were tested with 50 mL of sorption solution containing 10 µg L^{-1} of PGMs. After sorption followed elution of PGMs with 10 mL of organic solvent or organic solvent in the presence of 1 mol L^{-1} HCl. The organic solvent was then evaporated from elution solution on electric hot plate and residue was supplemented to a 10 mL volumetric flask by 1 mol L^{-1} HCl. The enrichment factor was 5. For optimization of preconcentration were simultaneously sorbed four parallel solutions under the same conditions. Resulting values of recoveries were averaged and relative standard deviation of recovery was calculated. All results of recoveries are given in % of recoveries and were compared to five times the signal of intensity of a reference sample (solution with 10 µg L^{-1} of PGMs in 0.1 mol L^{-1} HCl).

RESULTS AND DISCUSSION

Optimization of sorption. For the optimization purposes, the influences of pre-treatment of column (conditioning of sorbent) by complexing agents or surfactants, combination of complexing agents with surfactants, concentration of complexing agents in sorbed solutions, acidity of sorbed solutions and influence of surfactant concentration in conditioning solution were studied.

Pre-treatment of SDB-L sorbent was performed using conditioning by various complexing agents, such as ammoniumpyrrolidindithiocarbamate (APDC), thiourea (TU), 4-(2-pyridylazo)resorcinol (PAR) and 8-hydroxyquinoline-5-sulfonic acid (8-HQS) or by using various cationic surfactants: benzyldimethyltetradecylammonium chloride (Zephyramine®), N-(α-karbethoxypentadecyl)trimethylammonium bromide (Septonex®) and benzyldimethyl-dodecylammonium bromide (Ajatin®). The results are shown in Table number 2. Among them, it is evident that conditioning of the sorbent using complexing agents is not appropriate. In contrast conditioning by cationic surfactant can be advantageously used.

Because the sorbent conditioning by complexing agent prior to the sorption of platinum group metals was not successful, was tested by conditioning with cationic surfactant and in the presence of complexing agents in sorbed solution. They were all tested combinations of cationic surfactants and agents. Sorption was carried out under similar conditions as described below the

Table 2. All results are shown in Table 3. As is evident from the above results, it seems most appropriate combination Septonex® and 4-(2-pyridylazo)resorcinol (PAR). In this system, the recovery of sorption was about 100% both for platinum, palladium and osmium. This system was used for further optimization tests of sorption efficiency of platinum group metal sorbed on SDB-L.

The next step was to determine the optimal concentration of reagent PAR. Tested concentrations $2.5.10^{-6}$, 5.10^{-6}, 1.10^{-5} and $2.5.10^{-5}$ mol L^{-1} of PAR showed that the best results of sorption efficiency was achieved at 1.10^{-5} mol L^{-1} concentration. This amount of agent was used in the next experiments.

One of the other tested parameters during optimization process was an acidity of sorbed solution. Sorption of 50 mL with 10 μg L^{-1} of PGMs and 1.10^{-5} mol L^{-1} PAR in 0.1 mol L^{-1} HCl was carried out under optimal sorbent pre-treatment by 5.10^{-3} mol L^{-1} Septonex® and followed elution by acetonitrile with 1 mol L^{-1} HCl (4:1). Average recoveries show that under high pH (5-7) occurred to increasing sorption efficiency only for Rh and Ir. For platinum, palladium and osmium seems to be the best lower pH. As optimal acidity was selected pH 1 (caused by the presence of 0.1 mol L^{-1} HCl) in order to avoid adsorption of platinum group metal complexes on the volumetric flask wall at higher pH values. At pH 1 was achieved return sorption for Pt, Pd and Os, exceeding 95%.All other measurements are therefore carried out under conditions of pH 1.

To determine optimal concentration of surfactant were tested various concentrations of Septonex®, results are viewed in Table 4. The

TABLE 2
Sorption efficiency (%) for various pre-treatment of the sorbent.

	Ru	Rh	Pd	Os	Ir	Pt
Conditions 1						
APDC[a]	2.7±0.8	0.6±0.04	25.8±1.6	83.6±2.8	6.9±0.7	65.2±1.3
TU[b]	2.5±0.2	0.2±0.01	96.8±1.8	85.6±1.3	6.1±0.8	48.8±1.7
PAR[c]	0.5±0.03	0.1±0.01	94.4±3.7	14.3±1.3	5.6±0.7	6.4±0.3
8-HQS[d]	0.6±0.09	0.2±0.02	58.1±2.5	24.9±2.8	6.5±0.9	9.4±0.7
Conditions 2						
Zephyramine®	44.5±1.99	2.2±0.2	98.6±2.1	57.1±0.6	60.5±1.2	70.2±0.8
Septonex®	43.5±0.6	1.7±0.02	58.3±2.8	89.8±3.9	82.0±1.4	86.9±1.9
Ajatin®	42.3±1.6	1.4±0.03	96.7±1.9	29.8±0.5	64.4±0.4	55.9±0.2

[a]-Ammoniumpyrrolidindithiocarbamate, [b]-thiourea, [c]-4-(2-pyridylazo) resorcinol, [d]-8-hydroxyquinoline-5- sulfonic acid. **Conditions 1** – conditioning of sorbent by 10 mL of 5.10^{-6} mol L^{-1} of agent in 0.1 mol L^{-1} HCl. **Conditions 2** - conditioning of sorbent by 10 mL of 1.10^{-3} mol L^{-1} of cationic surfactant in 0.1 mol L^{-1} HCl. Followed sorption of 10 μg L^{-1} of PGMs in 0.1 mol L^{-1} HCl, elution by 10 mL acetonitrile with 1 mol L^{-1} HCl (4:1).

TABLE 3
Sorption efficiency (%) for various pre-treatment of the sorbent by cationic surfactants and in the presence of complexing agents in sorbed solutions.

	Ru	Rh	Pd	Os	Ir	Pt
Zephyramine®						
APDC[a]	43.5±1.3	3.7±0.07	24.8±0.2	73.6±1.4	46.2±1.4	93.9±0.9
TU[b]	42.5±0.8	2.3±0.1	61.3±3.4	95.4±0.9	57.0±1.0	91.2±0.7
PAR[c]	41.6±1.2	1.9±0.1	88.0±4.6	71.0±0.6	48.5±0.7	86.5±0.9
8-HQS[d]	44.7±1.7	1.8±0.1	78.6±3.4	58.9±0.6	72.9±1.0	84.6±0.8
Septonex®						
APDC[a]	44.9±1.3	1.6±0.08	19.3±0.4	91.4±1.0	36.5±2.2	98.9±1.8
TU[b]	42.2±1.8	1.1±0.04	97.9±2.7	73.8±1.0	29.6±1.2	57.8±1.6
PAR[c]	**41.4±1.3**	**1.1±0.04**	**99.4±2.9**	**96.9±3.1**	**42.5±1.0**	**99.4±1.7**
8-HQS[d]	40.4±1.6	1.1±0.09	98.1±4.4	62.4±1.5	24.0±0.4	88.2±1.8
Ajatin®						
APDC[a]	40.8±0.7	1.8±0.04	7.8±1.2	52.1±4.8	40.9±0.6	77.3±0.7
TU[b]	39.8±0.3	1.6±0.05	31.9±3.9	10.2±1.7	51.6±0.6	25.6±0.7
PAR[c]	43.1±0.5	1.7±0.05	80.0±2.5	18.0±0.6	51.7±1.1	40.5±1.6
8-HQS[d]	37.1±2.0	1.4±0.2	36.0±2.4	8.8±2.4	62.0±3.6	33.7±1.4

[a]-Ammoniumpyrrolidindithiocarbamate, [b]-thiourea, [c]-4-(2-pyridylazo) resorcinol, [d]-8-hydroxyquinoline -5-sulfonic acid. See conditions of sorptions under Table 2.

sorption conditions were following: conditioning of SDB-L sorbent by 10 mL of 1.10^{-4}, 5.10^{-4}, 1.10^{-3} or 5.10^{-3} mol L^{-1} Septonex® in the presence of 0.1 mol L^{-1} HCl, sorption of 50 mL solution with 10 μg L^{-1} of PGMs in 0.1 mol L^{-1} HCl in the presence of 5.10^{-6} mol L^{-1} 4-(2-pyridylazo) resorcinol (PAR). Elution was performed using 10 mL of mixture with acetonitrile and 1 mol L^{-1} HCl (4:1). The tested Septonex® concentrations showed that increasing concentrations increases the sorption efficiency. The concentration 5.10^{-3} mol L^{-1} this cationic surfactant Septonex® seems to be the best concentration. Higher concentrations were not tested because of possible contamination ICP-MS instrument.,

Optimization of elution. To determine the optimal elution efficiency were tested by series of eluents. The sorption was carried out under the following conditions: conditioning of sorbent by 10 mL of 5.10^{-3} mol L^{-1} Septonex® in 0.1 mol L^{-1} HCl, sorption of 50 mL solution with 10 μg L^{-1} of PGMs in 0.1 mol L^{-1} HCl in the presence of 5.10^{-6} mol L^{-1} 4-(2-pyridylazo) resorcinol (PAR). For elution was always used 10 mL of solution, presented in Table 5.

The most suitable eluent was mixture of acetonitrile and 1 mol L^{-1} HCl in the ratio 4:1 because of almost 100% recoveries for platinum (IV) and palladium (II).

After finding the optimal eluent mixture was also examined in detail the elution volume for the quantitative elution of the adsorbed platinum group metal complexes. The conditions of sorption were: conditioning of sorbent by 10 mL of 5.10^{-3} mol L^{-1} Septonex® in 0.1 mol L^{-1} HCl, sorption of 50 mL solution with 10 μg L^{-1} of PGMs in 0.1 mol L^{-1} HCl in the presence of 1.10^{-5} mol L^{-1} 4-(2-pyridylazo) resorcinol (PAR). For elution was used 10 mL of solution mixture of acetonitrile: 1 mol L^{-1} HCl (4:1) (see Table 5). To determine the elution curve was collected a total of 10 mL of elution mixture for each milliliter of separately. Thereafter, the individual fractions of the eluate were prepared similarly as above (evaporated on a hot plate and transfer to the 10 mL volumetric flasks). From the elution curve shown in Figure 1 is seen that the quantitative elution for all intercepted platinum group metal complexes occurs during the first five milliliters. For quantitative elution is recommended twice the amount of eluate, meaning 10 mL. This elution volume was used during each sorption.

TABLE 4
The effect of different Septonex® concentrations on average recoveries (%).

concentration[a]	Ru	Rh	Pd	Os	Ir	Pt
1.10^{-4}	8.0±0.5	0.2±0.03	63.8±1.7	51.4±1.6	13.2±0.5	52.5±1.9
5.10^{-4}	32.1±0.6	0.6±0.02	89.5±2.1	64.1±1.0	17.3±0.4	82.6±2.0
1.10^{-3}	38.1±1.7	0.7±0.08	98.6±3.0	71.3±0.8	18.5±0.4	97.4±0.5
5.10^{-3}	**43.2±0.8**	**2.5±0.6**	**99.9±1.5**	**73.5±0.2**	**46.6±4.1**	**101.7±1.8**

[a]–Concentration (mol L^{-1}) of Septonex® in conditioning solution

TABLE 5
Average recoveries (%) PGMs after elution by various solvents.

eluent	Ru	Rh	Pd	Os	Ir	Pt
ET[a]	39.0±0.8	0.8±0.1	44.7±0.7	87.0±1.9	24.4±0.4	66.9±1.9
AC[b]	43.0±0.7	0.9±0.09	95.5±2.7	76.4±1.2	19.5±1.2	80.2±1.3
ACN[c]	35.7±0.5	0.9±0.09	71.0±1.7	95.9±2.9	21.6±0.4	78.6±0.5
ET:AC (1:1)	36.2±0.2	0.6±0.07	77.4±1.3	55.6±0.7	16.2±0.2	73.2±1.3
ET:ACN (1:1)	38.8±0.6	0.9±0.1	76.0±2.8	43.7±1.5	12.3±0.8	72.5±0.8
AC:ACN (1:1)	41.7±0.9	0.8±0.08	93.9±2.6	71.1±2.5	13.5±1.4	89.0±1.4
ET:HCl[d] (4:1)	42.7±1.1	1.4±0.2	58.7±1.9	68.4±1.7	21.5±1.4	94.3±1.8
AC:HCl (4:1)	40.4±0.3	1.3±0.3	89.5±2.4	66.3±0.9	43.3±1.2	99.4±0.9
ACN:HCl (4:1)	**40.0±0.3**	**1.0±0.1**	**99.8±0.4**	**93.3±1.2**	**32.0±1.7**	**99.0±0.6**
ET:AC:HCl (2:2:1)	41.9±0.3	1.1±0.1	83.5±1.2	67.9±1.4	28.8±0.1	98.8±1.7
ET:ACN:HCl (2:2:1)	45.4±0.9	1.1±0.06	88.2±2.4	68.1±1.3	30.1±1.7	100.6±2.5
AC:ACN:HCl (2:2:1)	45.4±0.8	1.2±0.09	89.8±1.9	69.0±1.1	33.2±0.6	98.8±1.7

[a]–ET absolute ethanol, [b]–AC acetone (concentrated), [c]–ACN acetonitrile (concentrated), [d]–hydrochloric acid with concentration 1 mol L^{-1}.

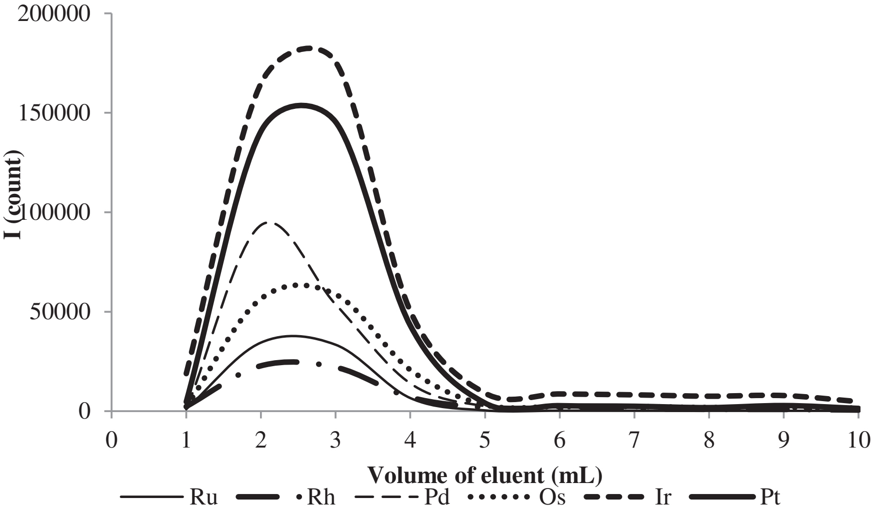

FIGURE 1
Elution curves for all platinum group metals.

Effect of foreign ions. The effect of various concentrations of selected cations, anions and their mixtures to the sorption efficiency of the platinum group metals was studied. The sorption was carried out under optimal conditions. Selected individual ions were Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Cl^-, NO_3^-, SO_4^{2-}, $PO_4^{3-}$and CO_3^{2-}. To the amount of platinum group metals in sorbed solution were calculated excess of interfering ions 1:100, 1:1000, 1:2500 and 1:10000, which corresponds to the range concentrations 1.10^{-5}, 1.10^{-4}, $2.5.10^{-4}$ and 1.10^{-3} mol L^{-1} of ions. Also tested were mixed standard solutions containing Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Ti^{4+}, Zn^{2+} and mixture of anions, such as Br^-, Cl^-, F^-, NO_3^-, SO_4^{2-}, $PO_4^{3-}$and SO_4^{2-} both in the excess 1:100 and 1:1000 against to platinum group metal concentrations.

No interference was observed for platinum and palladium in all tested conditions in the presence of various ions or their combinations. Only osmium showed reduce sorption efficiency to 60% and the other platinum group metals recoveries remained unchanged.

Real samples of water and lichens. This sorption system was developed for the analysis of real samples from the environment. There were tested three types of real samples – river water, peat bog water and lichens (class *Hypogymnia physodes*). In these samples, we unexpected the presence of platinum group metals because of their origin from the Šumava National park in Czech Republic. They have been used as a real matrix for verifying the effectiveness of the sorption of platinum group metals for the analysis of real samples, under real conditions.

The samples of water and lichens were treated as described in section 2.3. After this, sorption under optimized conditions was applied conditioning of SDB-L in plastic cartridge sorbent by 10 mL of 5.10^{-3} mol L^{-1} of Septonex® in 0.1 mol L^{-1} HCl, sorption of 50 mL real sample solution with 10 μg L^{-1} of PGMs in 0.1 mol L^{-1} HCl in the presence of 1.10^{-5} mol L^{-1} 4-(2-pyridylazo) resorcinol (PAR). For elution was used 10 mL of solution mixture of acetonitrile : 1 mol L^{-1} HCl (4:1). The recovery results demonstrate that the matrix of real samples no affects the success of the SPE and the process may therefore be used for their analysis regard to the content of platinum metals.

After finding no matrix effect of lichens on recoveries of sorption for platinum group metals, the samples of lichens *Hypogymnia physodes* were exposed to the exhaust gases near the busy road in the city of Brno. Traffic frequency of this road is average about 16,000 vehicles per 24 hours.

TABLE 6
The contents of platinum group metals (μg kg^{-1}) in lichen samples.

Samples	Ru	Rh	Pd	Os	Ir	Pt
Exposed lichens[1]	< LOD	< LOD	< LOD	< LOD	721.4	187.9
Exposed lichens[2]	168.9	< LOD	397.1	1534.5	748.9	246.0

[1] Direct determination by ICP-MS, [2] ICP-MS determination after SPE on SDB-L sorbent.

Samples of lichens were installed in strainers (about 10 g) using the dry bag technique and placed on the crash barrier. The time exposure of these samples was three months. After this the samples were collected, weighted 0.25 g of lichens and pre-treated as described in section 2.3. Than followed the sorption on SDB-L sorbent under optimized conditions. The quantity of determined platinum group metals in sample of blank and in exposed samples were shown in Table 6. For comparison is shown the direct determination (^{1}) of platinum group metals in pre-treated samples and determination which preceded the solid phase extraction (^{2}) for separation of matrix effect and preconcentration of determined metals. This experiment, preceded by the determination of blanks, that was determination of uncontaminated samples of lichens by direct measurement and determination after the sorption procedure. All measured values of blanks lying below the detection limits for platinum group metals.

CONCLUSIONS

The preconcentration technique SPE of platinum group metals on Amberlite polystyrene-divinylbezene based sorbent (Strata SDB-L) was optimized. There were tested conditions for pre-treatment of sorbent, conditioning, conditions for the sorption process and was found optimal elution. The optimum for the sorption of platinum group metals appears following: conditioning of sorbent by 10 mL of 5.10^{-3} mol L^{-1} Septonex® in 0.1 mol L^{-1} HCl, sorption of 50 mL solution with 10 μg L^{-1} of PGMs in 0.1 mol L^{-1} HCl in the presence of 1.10^{-5} mol L^{-1} 4-(2-pyridylazo) resorcinol (PAR). For elution with success was used 10 mL of solution mixture of acetonitrile: 1 mol L^{-1} HCl (4:1). Under these conditions 100% recoveries has been achieved for platinum, palladium and osmium. The sorption efficiency for ruthenium and iridium were about 40% and rhodium is not possible preconcentrated by this method of SPE.

In the analysis of real samples the matrix effect has been detected for river and peat bog water and for decomposed samples of lichens *Hypogymnia physodes*. The samples of lichens *Hypogymnia physodes* were exposed to the exhaust gases near the busy road in the city of Brno, installed in strainers (about 10 g) using the dry bag technique and placed on the crash barrier. The time exposure of these samples was three months and following the application of optimized SPE method. During the direct determination only iridium and platinum were detected. After optimized SPE methods also the others platinum group metals were determined.

Thus, this procedure can successfully be used for evaluating the content of the platinum group metals, especially Platinum and Palladium, in environmental samples.

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REFERENCES

[1] Ravindra, K., Bencs, L., Van Grieken, R. (2004) Platinum group metals in the environment and their health risk. The Science of the Total Environment 318, 1-43.
[2] Reith, F., Campbell, S.G., Ball, A.S., Pring, A., Southam, G. (2014) Platinum in Earth surface environments. Earth-Science Reviews 131, 1-21.
[3] Jackson, M.T., Sampson, J., Prichard, H.M. (2007) Platinum and palladium variations through the urban environment: Evidence from 11 sample types from Sheffield, UK. The Science of the Total Environment 385, 117-131.
[4] Lesniewska, B.A., Godlewska-Zylkiewicz, B., Bocca, B., Caimi, S., Caroli, S., Hulanicki, A. (2004) Platinum, palladium and rhodium content in road dust, tunnel dust and common grass in Bialystok area (Poland): a pilot study. Science of the Total Environment 321, 93-104.
[5] Wang, J., Zhu, R., Shi, Y. (2007) Distribution of platinum group elements in road dust in the Beijing metropolitan area, China. Journal of Environmental Sciences 19, 29-34.
[6] Pawlak, J., Lodyga-Chruscinska, E., Chrustowicz, J. (2014) Fate of platinum metals in the Environment. Journal of Trace Elements in Medicine and Biology 28, 247-254.
[7] Bencs, L., Ravindra, K., Van Grieken, R. (2011) Platinum: Environmental Pollution and Health Effects. Reference Module in Earth Systems Sciences from Encyclopedia of Environmental Health, Elsevier, 580-595.
[8] Platinum, Environmental Health Criteria 125 (1991) World Health Organization, Geneva, 1-139.
[9] Bencs, L., Ravindra, K., Van Grieken, R. (2003) Methods for the determination of platinum group elements originating from the abrasion of automotive catalytic converters. Spectrochimica Acta Part B 58, 1723-1755.
[10] Komendova-Vlasankova, R., Sommer, L. (2002) Separation and preconcentration of platinum group metals and gold on modified silica and XAD sorbents in the presence of cationic surfactants for their determination by ICP-AES. Collect. Czech. Chem. Commun. 67, 454-469.
[11] Ljubomirova, V., Djingova, R. (2008) Speciation of inorganic platinum-chloride complexes in spiked environmental samples by

SPE and ICP-AES. Anal. Chim. Acta 614, 119-126.

[12] Guidelines for data acquisition and data duality evaluation in environmental chemistry (1980). Analytical Chemistry 52, 2242-2249.

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The HR-CS-GF-AAS determination and preconcentration of palladium in contaminated urban areas, especially in lichens[☆]

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ABSTRACT

The increasing content of platinum group metal particles emitted into the environment by car traffic is gradually attracting the attention of the scientific community. However, the methods for the determination of platinum group metals in environmental matrices are either costly or suffer from low sensitivity. To facilitate the use of less sensitive, but significantly cheaper, devices, the preconcentration of platinum group metals is employed. For platinum, a multitude of preconcentration approaches have been published. On the contrary, the preconcentration approaches for palladium are still rare. In this work, the development, optimization, and testing of a new approach is described; it is based on a preconcentration of palladium on octadecyl modified silica gel together with the complexing agent dimethylglyoxime, and it is then analyzed with the high-resolution continuum-source atomic absorption spectrometry. For comparison, a newly developed sorbent, QuadraSil™ TA, with a high affinity for platinum group metals was also tested. The preconcentraiton approach was tested on the lichen *Hypogymnia physodes*, which served as a bioindicator of palladium emissions. The case study site was a mid-sized city in central Europe: Brno, Czech Republic. The dry "bag" monitoring technique was used to collect the palladium near roads with a large span of traffic density. The developed analytical approach confirmed an increasing concentration of palladium with increasing exposure time and intensity of the traffic. Consequently, a simple relationship between the amount of bioaccumulated palladium and traffic density was established.

1. Introduction

Increasing concentrations of platinum group metals (PGMs), mainly platinum (Pt) and palladium (Pd), have been observed throughout the environment over the last twenty years. Naturally, Pd occurs together with other platinum metals in very low concentrations (0.015 mg kg^{-1} Pd and 0.010 mg kg^{-1} of platinum) (Reith, Campbell, Ball, Pring and Southam, 2014). Anthropogenic Pd have been reported in various environmental compartments such as airborne dust, aerosols, road and tunnel dust, soil, aquatic environments, sediments, plants, body fluids, and animal tissues (Ravindra, Bencs and Van Grieken, 2004). The sources of Pd include dentistry, the chemical industry, electronics, fuel cells, jewelry, and surgical tools (Garoufis, Hadjikakou and Hadjiliadis, 2009), with the largest source being the automotive industry in which Pd is one of the main components of road vehicle catalysts (Melber, Keller and Mangelsdorf, 2002); (Twigg, 2011). Together, Pt and Rh form an active catalytic layer that catalyzes the conversion reactions of toxic exhaust gases coming from the fuel combustion process into less toxic products. Globally, gasoline cars represent more than 85% of the total use of Pd in autocatalysis and its use is increasing ("Johnson Matthey", 2019); (Rosner, Coenen-Stass and König, 1991). The PGMs or their oxides are released from the catalysts in the form of elementary nanoparticles (Komendová, Žídek, Berka, Jemelková, Řezáčová, Conte and Kučerík, 2019) with a size below 0.3 μm; they are released into the environmental compartments nearby roads with high traffic due to the high temperature of flue gas, mechanical abrasion, the influence of a catalyst's poisons, the age of the catalyzer, and the riding style of car (Prichard and Fisher, 2012); (Goncalves, Domínguez and Alvarado, 2008). As a result, the most effected sites are urban agglomerations that have the highest car traffic (Komendova and Jezek, 2018); (Kosarova, Komendova and Skeril, 2015). The PGMs are already considered to be a global environmental pollution due to their easy transport upon

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solubilization (Rauch, Hemond, Barbante, Owari, Morrison, Peucker-Ehrenbrink and Wass, 2005); (Ek, Morrison and Rauch, 2004). The solubilization is influenced by air turbulence caused by passing vehicles or from strong winds, as well as by other climatic conditions, the morphology of the local terrain, and the presence of barriers like higher plants (Goncalves, Domínguez and Alvarado, 2008). The occurrence of PGMs depends not only on the particular concentration but also on the form of the occurrence, the bioavailability, the solubility, and the mobility of metals. The concentration of platinum group metals released from automotive catalysts are in the magnitude of ng.km^{-1}, pg. m^{-3} in the air, road dust, soil, vegetation and in the animal body in ng.g^{-1} (Melber, Keller and Mangelsdorf, 2002), and the concentrations are steadily increasing (Ravindra, Bencs and Van Grieken, 2004). Unlike other metals, the toxicological information about Pd is not yet clear. Palladium and its compounds may cause medical complications such as allergic reactions, asthma, nausea, hair loss, skin and eye irritation, or other autoimmune disorders. Overall, clinical findings are not yet significant (Kielhorn, Melber, Keller and Mangelsdorf, 2002); (Faurschou, 2011).

An important group of monitored contaminated environmental components are plants. Both passive biomonitoring (e.g. grass or tree bark in the immediate vicinity of transport roads) and active biomonitoring (e.g. moss or lichen) are used to monitor the amount of PGMs. Pd is the most soluble of the PGMs, therefore it is also very mobile and has the greatest potential to be absorbed into living organisms. In plants, the largest amount of Pd was found in the root system. Palladium is transformed into biological materials through roots by binding to a sulfur-rich low-molecular substance (Wiseman and Zereini, 2009).

Biomonitoring is frequently used to determine the possibility of toxic metals entering biotic material. The most common bioindicators for the determination of environmental pollution by heavy metals are mosses, lichens (Pino, Alimonti, Conti and Bocca, 2010), ferns, grasses, tree bark, and needles (Szczepaniak and Biziuk, 2003); (Aničić, Tomašević, Tasić, Rajšić, Popović, Frontasyeva, Lierhagen and Steinnes, 2009).

Due to the relatively low concentration of PGMs in environmental matrices, their analysis requires either the use of costly techniques such as ICP-MS, or of the technique sample preconcentration, which enables the use of less expensive techniques such as AAS with flame atomization or atomization in a graphite cuvette. The next benefit of preconcentration is the separation of the matrix, which could interfere with the analyte detection. Up to now, the preconcentration has widely been used in the analysis of PGMs in environmental samples such as natural and waste water, soil, dust, atmospheric fallout, biological materials of plant and animal origin, and food. However, the preconcentration methods were developed mainly for platinum, and palladium was rather neglected.

For the separation of palladium, the most commonly used solid sorbents are modified polymer Amberlite resin (Kimuro, Gandhi, Kunda, Hamada and Yamada, 2017), polyurethane foam (Moawed, 2006), activated carbon (Sharififard, Soleimani and Ashtiani, 2012), modified silica gel C18 (Komendova-Vlasankova and Sommer, 2002); (Tokalıoğlu, Oymak and Kartal, 2004); (Komendova, Nevrla, Kuta and Sommer, 2016) and a variety of newly developed sorbents, e.g. ion-imprinted polymer nanoparticles (Ghorbani-Kalhor, Behbahani and Abolhasani, 2015), magnetic metal-organic framework (MOF) (Bagheri, Taghizadeh, Behbahani, Akbar Asgharinezhad, Salarian, Dehghani, Ebrahimzadeh and Amini, 2012), nanoporous silica MCM-41 (Behbahani, Najafi, Amini, Sadeghi, Bagheri and Hassanlou, 2014a) and polypropylene amine dendrimers (POPAM)-grafted multi-wallet carbon nanotubes (MWCNTs) (Behbahani, Gorji, Mahyari, Salarian, Bagheri and Shaabani, 2014b).

The aim of this work was 1) to develop a new preconcentration method for the determination of palladium in lichens, based on a C18 silica gel modified with dimethylglyoxime and including experimental conditions such as a selection of appropriate sorbents, solvents, and eluents with respect to the method of the final analysis, 2) to validate the method and compare it with selective sorption sorbent QuadraSil™ TA bound triamine (Nakajima, Ohno, Chikama, Seki and Oguma, 2009), 3) to use the newly developed approach to assess the actual contamination of air by palladium in a mid-sized city of central Europe (Brno, Czech Republic).

2. Materials and methods

2.1. Chemicals, reagents, sorbents, and reference material

For the optimization conditions of the AAS and preconcentration method was used certified reference material of calibration standard solution ASTASOL ® with concentration of Pd 1 ± 0.002 g l^{-1} in 5% HCl, Fe standard solution with 1 ± 0.002 g l^{-1} in 5% HCl and mixture ASTASOL-Mix ® consisted of Cd(II), Co(II), Cu(II), Cr(III), Mn(II), Ni(II), Pb(II), V(V), Zn(II) with concentration 100.0 ± 0.5 mg.L^{-1} in 5% HNO_3, all from Analytika Ltd., Czech Republic (http://www.analytika.net).

Dimethylglyoxime (diacetyldioxime) was purchased from Sigma-Aldrich (https://www.sigmaaldrich.com) and all used chemicals were of analytical reagent grade.

500 mg of silica gel C18 Bond Elut sorbent (Agilent Technologies) with average particle size 44–60 μm, specific surface area 460–520 m^2. g^{-1}and average pore diameter 60–87 Å were placed in 3 mL cartridges.

The 250 mg of selective sorbent QuadraSil™ Triamine TA (Sigma-Aldrich), with average particle size 20–100 μm, was filled into new empty 3 mL Bond Elut column Agilent Technologies (https://www.agilent.com) equipped with bottom and top frits.

The SILICA-cart column consists of a filled 1 mL polypropylene cartridge (Tatren PD 140) packed with 60 μm spherical silica TESSEK (http://www.tessek.com) Separon SGX sorbent.

The Standard Reference Material of tunnel dust BCR-723 (JCR Joint Research Centre) with determined platinum metal content (Sutherland, 2007) was used to verify the entire analysis procedure: the sample decomposition, the preconcentration technique, and the final Pd determination by HR–CS–GF-AAS. Certified Pd concentration in BCR-723 was declared in the ratio 6.1 ± 2.5 ng g^{-1}. The measured values 5.770 ± 2.022 ng g^{-1} were in good agreement with the certified Pd content.

2.2. Lichen samples, sampling, and pre-treatment

In this work, the applied form of active biomonitoring was called dry “bag” monitoring, a technique that uses lichen (*Hypogymnia physodes*) as a bioindicator. Lichens are poikilohydric organisms that are able to withstand harsh environmental conditions and stress factors. They have root systems that breathe through their entire body surface, allowing for a large degree of absorption of hazardous elements (Pino, Alimonti, Conti and Bocca, 2010); (Huang, Xiang, Wang, RenJohnsonDavid, and Xu, 2019); (Kłos, Ziembik, Rajfur, Dołhańczuk-Śródka, Bochenek, Bjerke, Tømmervik, Zagajewski, Ziółkowski, Jerz, Zielińska, Krems, Godyń, Marciniak and Świsłowski, 2018); (Hoffman, Rattner, Burton, Jr. and Cairns, Jr., 2003). Most commonly, this method is used to capture dust and aerosols as well as to deposit metals or other pollutants in urban and industrial areas (Conti and Cecchetti, 2001); (Aničić, Tomašević, Tasić, Rajšić, Popović, Frontasyeva, Lierhagen and Steinnes, 2009).

Hypogymnia physodes was sampled from the bark of the tree *Pices abies* from the protected nature area Beskydy. The nearest third-class road is more than 5 km away. There was no inhabited area, roads or industry surrounding the sampling site. The Pd content in these samples was below the limit of detection. These organisms were then placed in mesh polyethylene bags (0.5 cm mesh size) and attached to road barriers beside nine roads with heavy traffic. The sampler consisted of three parts, the first of which was collected and analyzed after 90 days, the second part after 120 days, and the third after 150 days. These bags were located at different traffic-busy roads in the city of Brno. The sampling site locations for the placement of the "bags" were selected in consideration of the frequency of car traffic. These sites were all located in the city of Brno, Czech Republic. Details of the sampling sites are reported in Table 1.

Samplers were fixed using plastic tape to the road barrier. After exposure, the bags were dried at room temperature. Before the decomposition process, the content of the bag was deprived of the protective breathable nets, and the contents were quantitatively transferred into glass flasks. The decomposition of the lichen was performed by boiling it in *aqua regia*. The portion of the lichen sample (5—10 g) was quantitatively transferred into a round bottom flask and wetted with 15 mL of HNO3. The sample was left in a nitric acid until the next day, at which point 45 mL of HCl was added; the volume of the flask was then fed through a heating mantle to reach boiling temperature. After 2 h at reflux, 25 mL of water was added to the mixture, and the whole volume of the flask was boiled for 15 min. Followed by filtration, the mixture evaporated on a hot plate and the quantitative conversion decomposed the sample into a 50 mL volumetric flask.

2.3. Instrumentation

Optimization of the method and analysis of lichen samples was performed on the atomic absorption spectrometer contrAA® 800 D from Analytik Jena (Germany) with a continuous radiation source and high-resolution monochromator, with uses an Xe lamp across the entire spectrum with the possibility to use any atomic absorption line or molecular band for the determination of the elements. The spectrometer simultaneously solves background correction and stability by using Iterative Background Correction (IBC). The optical system consists of a high-resolution Echelle monochromator and a sensitive CCD detector. For the determination of Pd, the graphite cuvette atomization was chosen to provide lower detection limits.

For the determination of Pd, was selected primary line 244.791 nm with 100% relative sensitivity. Optimal measurement parameters of the temperature program were: drying 1 at 80 °C, drying 2 at 90 °C, drying 3 at 110 °C, pyrolysis 1 at 350 °C, pyrolysis 2 at 950 °C, atomization at 2200 °C, and cleaning at 2450 °C. Under these optimal conditions, the Limit of Detection (LOD) was 1.110 µg.L^{-1} and the Limit of Quantification (LOQ) was 3.329 µg l^{-1}. The instrumental LOD and LOQ were calculated on the basis of the 3sigma definition (Shrivastava and Gupta, 2011) and were evaluated from 10 measurements of the blank solutions:

$$\mathrm{LOD/LOQ} = \mathrm{FxSD/b}$$

F: factor 3 or 10 for LOD and LOQ, respectively,
SD: standard deviation of the blank
b: slope of the regression line

All results obtained in this research are the average of three separate independent determinations and were each measured five times on the atomic absorption spectrometer.

For the preconcentration of Pd, the sorption apparatus was used, consisting of a pump 82.4 PCD with four cassettes ISMATEC ISO649 through which the solutions using silicone tubing were sorbed on the cartridges with the selected sorbent. These cartridges were connected to the vacuum system, J. T. Baker, SPE-12G.

2.4. Preconcentration procedures

2.4.1. Preconcentration on silica gel with dimethylglyoxime

Octadecyl modified silica gel C18 is the most widely used nonpolar sorbent. The sorption of metal ions requires modifying its surface by adsorption of an amphiphilic chelating agent which can easily interact with metal ions giving rise to the organo-metal complex. The chelating agent used in this work was dimethylglyoxime (DMG) which is among the most selective agents for transition metals such as Ni(II) and Pd(II). In the PGMs, only Pd in the presence of HCl is precipitated with DMG, giving a yellow Pd:DMG 1:2 complex. The complex is insoluble in water and dissolves in the presence of ammonia. This complex is formed even at a small amount of mineral acid and is the only form in which DMG stable precipitates in the medium with pH 1. X-ray analysis revealed a square-planar structure wherein two ligands are connected by the strong intramolecular hydrogen bond, stabilizings

Table 1
Characterization of sample collection places.

Sample number	Places of sampling	Traffic intensity (thousands of cars/24 h)[a]	GPS
1	D2 motorway	50	49°9′17.185″N, 16°37′47.436″E
2	Sportovní Street	45	49°13′1.656″N, 16°36′15.039″E
3	Tomkovo Square	40	49°12′47.963″N, 16°38′16.412″E
4	Hradecká Street [b]	35	49°13′47.300″N, 16°34′48.300″E
5	Otakara Ševčíka Street	35	49°11′27.825″N, 16°38′54.364″E
6	Hradecká Street [c]	25	49°13′47.759″N, 16°34′47.560″E
7	Koliště Street	20	49°11′35.136″N, 16°36′57.035″E
8	Poříčí Street	20	49°11′11.716″N, 16°35′44.651″E
9	Kotlářská Street	15	49°12′24.625″N, 16°36′3.952″E
10	Traffic free location	0	49°22′43.342″N, 16°66′75.894″E

[a] ("Road and Motorway Directorate of the Czech Republic. Traffic census.", n. d.).
[b] Downtown.
[c] From city.

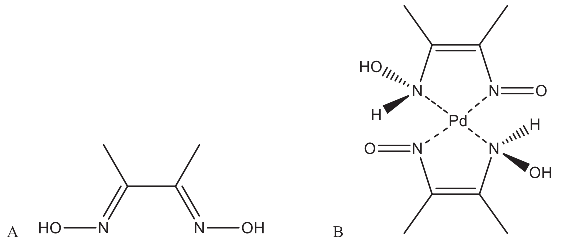

Fig. 1. A dimethylglyoxime, B Bis(dimethylglyoxime)palladium.

the complex in a ratio of 1:2 metal:ligand (Fig. 1) (Panja, Bala, Pal and Ghosh, 1991). In addition, in the solid state, the complexes with nickel, palladium, platinum, and gold appeared to be stabilized by metal-metal interactions, with copper being the most complex stabilization by metal-oxygen bonds.

The separation of Pd based on the formation of the $Pd(DMG)_2$ complex was used in this work. The method was inspired by the results of (Tokalıoğlu, Oymak and Kartal, 2004) who used sorption dimethylglyoxime on bare silica sorbent, with only 40.80% sorption efficiency at pH 1.0. The available literature data sources showed that successful sorption should be carried out at $pH = 4.0$. However, under these conditions, in our work, we achieved the efficiency of only 65.40%. Therefore, instead of bare silica, silica gel modified with octadecyl C18 was chosen for this work because it was assumed to have a strong affinity to $Pd(DMG)_2$.

2.4.2. Preconcentration on QuadraSil™ TA sorbent

The newly developed approach based on the $Pd(DMG)_2$ complex was compared with the commercially available sorbent QuadraSil™, which is a registered trademark of the company Johnsons & Matthey. Chemically, it is a modified silica that, due to its steric properties, is highly selective for the reuptake of metal ions. QuadraSil™ is very robust, it is chemically, mechanically, and thermally resistant, spherically shaped and poorly swellable. Commonly, the particles have 54 μm. In this work, the QuadraSil™ TA triamine (Fig. 2) was used and the parameters of the preparation procedure were obtained from an article (Nakajima, Ohno, Chikama, Seki and Oguma, 2009).

3. Results and discussion

3.1. Development preconcentration method and testing of modified silica gel C18

The optimization of the parameters under conditions described in the chapter Materials and Methods for silica gel modified octadecyl chain showed a 100.30 ± 1.5% recovery of the Pd complex with dimethylglyoxime from the sorbed volume in the range of 10–1000 mL. As the final volume was 10 mL, the pre-concentration factor thus reaches 100. In addition, the factor can even be increased by evaporating the resulting eluate to lower volumes.

The mechanisms of sorption can be explained as follows: the free hydroxyl groups occurring on C18 are dissociated, hydrogen cation and a molecule complex of $Pd(DMG)_2$ are more easily bonded. To ensure the formation of the $Pd(DMG)_2$ complex, a selective agent must always be present in excess in comparison to the Pd. In this work, it was found that the best sorption results were achieved when the $Pd(DMG)_2$ complex was already formed in the solution before it was adsorbed to the distilled water wetted sorbent. On the contrary, when the sorbent was conditioned by the DMG, and the pure Pd solution was sorbed, the sorption was not quantitative. This may be due to an insufficient amount of the sorbed agent or a flow rate that was too high during sorption.

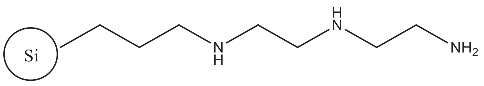

Fig. 2. QuadraSil™ TA triamine.

During optimization, the elution procedure was tested following eight eluent solutions: 1 mol.L^{-1} HCl in absolute ethanol, absolute ethanol, 1 mol.L^{-1} HCl in ethanol (denatured), ethanol (denatured), 1 mol.L^{-1} HCl in acetone, acetone, 1 mol.L^{-1} HCl in acetonitrile and acetonitrile. The best results were achieved using 1 mol.L^{-1} HCl in absolute ethanol. When studying the effect of acidity on the sorption process, it was found that 0.1 mol.L^{-1} HCl is the optimal medium concentration.

For the assessment of interferences of the sorption, the influence of ions and metals was tested, the presence of which can be expected in a matrix of real samples or which can be sorbed on the lichen together with Pd from polluted environmental matrices. Solutions containing anions (NO_3^-, SO_4^{2-}), common cations (Al^{3+}, Ca^{2+}, NH_4^+, Mg^{2+}, K^+, Na^+, Mn^{2+}), and heavy metal cations (Cd(II), Co(II), Cu(II), Cr(III), Mn(II), Ni(II), Pb(II), V(V), Zn(II), Fe(II)) were prepared. The influence was tested for 100- and 1000-times excess of the concentration of these ions in comparison with Pd. It was found that the 100-fold higher concentration of anions containing sulfates and nitrates had no influence on the sorption of Pd. However, the same number of common cations and heavy metal cations caused a slightly positive interference, but the average value never exceeded 110% of the limit of the Pd sorption efficiency. In contrast, a 1000 times higher concentration of anions and cations caused slightly negative interferences, but the mean values did not fall below 90% of the efficiency of sorption. Therefore, the results showed a good reliability of sorption of $Pd(DMG)_2$ complex on C18 modified silica.

After optimization of the sorption process was completed, the sorption parameters in which 100% recovery for Pd was achieved were found to be: a flow rate of sorption of 1 mL min^{-1}, a rinsing sorbent 10 mL of distilled water, the sorption of the Pd solution with the addition of agents DMG at the concentration of 3.44 mmol.L^{-1} in 0.1 mol.L^{-1} HCl, rinsing 5 mL of distilled water prior to the elution, and finally an elution using 10 mL of 1 mol.L^{-1} HCl in absolute ethanol. The eluate was further processed as follows: it was transferred to a Teflon™ dish, evaporated to near dryness on a hot plate, and then the residue was dissolved in 0.1 mol.L^{-1} HCl, quantitatively transferred to a 10 mL volumetric flask, and filled to the mark by using 0.1 mol.L^{-1} HCl.

3.2. Comparison of developed method with preconcentration on QuadraSil™ TA

The preconcentration on QuadraSil™ TA was performed according to the article by (Nakajima, Ohno, Chikama, Seki and Oguma, 2009). The authors used 100 mg of sorbent in an on-line arrangement to the ICP-AES preconcentration method. Therefore, the method had to be optimized for the conditions used in this work and the efficiency of Pd sorption on the amount of QuadraSil™ TA was tested. It was found that the highest efficiency of Pd sorption 98.5 ± 1.5% was achieved for 250 mg of sorbent, while 100 mg achieved only 92.7 ± 1.7%.

The mechanism of the sorption can be explained as follows: the amine functional group of diethylenetriamine shows a high selectivity for Pd in the presence of hydrochloric acid. The low pH maintains the Pd in solution in the form of chlorides or as a complex which interacts with the amine.

In this work, the effect of HCl concentration on the efficiency of Pd sorption was assessed. The highest sorption efficiency was observed at 0.1 mol.L^{-1} HCl.

For the elution of Pd from the QuadraSil™ TA sorbent, the appropriate eluent is thiourea (Nakajima, Ohno, Chikama, Seki and Oguma, 2009), but its optimum concentration had to be tested. The elution was performed at five different thiourea concentrations. The best results were obtained for 0.05 mol.L^{-1} thiourea as an eluent.

For the assessment of interfering effects on the sorption efficiency by ions and metals, inorganic cations and anions were used in this work, which presumably occur in environmental samples. Thus, mixed solutions of anions, cations, and metals were prepared and tested. The results suggested that 100- and 1000-times excess of cations Al^{3+}, Ca^{2+}, NH_4^+, Mg^{2+}, K^+, Na^+ and Mn^{2+} have almost no effect on the Pd sorption. However, the same amount of anions such as SO_4^{2-} and NO_3^- have 100 times higher content of metal cations such as Cd(II), Co(II), Cu(II), Cr(III), Mn(II), Ni(II), Pb(II), V(V), Zn(II) and Fe(II) and caused a significantly negative interference. In other words, it appeared that the QuadraSil™ TA sorbent is also an effective sorbent for other metal ions.

Therefore, the sorbent QuadraSil™ TA is not applicable for the preconcentration of Pd in the case of environmental matrices containing heavy metal ions and some anions because they violate the selectivity of the sorbent to Pd. For this reason, all the analyses of real samples were carried out by sorption on C18 silica gel (see next chapter) with a higher sorption efficiency and lower influences of accompanying ions.

3.3. *The determination of palladium in lichens exposed to air pollution in a mid-sized city of central Europe*

As aforementioned, the method based on the formation of $Pd(DMG)_2$ complex sorbed on C18 modifed silica was used for the assessment of the Pd contamination in Brno, which is representative of a mid-sized city with moderate traffic in central Europe. In total, Pd was determined in 30 ″bag” samples distributed all around the city. All samples were pre-treated using the above-described method and Pd was determined by using atomic absorption spectrometry.

All data measured by analyzing the Pd concentration in the lichen *Hypogymnia physodes* using this technique are reported in Table 2. For a better illustration, the data are also plotted in Fig. 3, where the density of the car traffic in the measured sites is also displayed.

The results confirmed the assumption that the amount of Pd will increase with the increasing sample exposure time in all localities. In addition, Fig. 3 indicates that the relative increase in Pd per traffic density increases with the length of exposition, which means that after 150 days the saturation of the lichen sorption capacity was still not reached. This is supported by Fig. 4, which reports the slopes of dependences of Pd concentration on exposition time for each sampling site with specific traffic car density. Accordingly, Fig. 4 represents a simple tool for prediction of Pd contamination in mid-sized cities. It is still questionable whether or not the data can be used in the prediction of Pd concentration in larger cities where the car traffic exceeds hundreds of thousands of cars per day.

Table 2
Palladium content in lichen (ng.g^{-1}).

Sample	Exposure		
	90 days	120 days	150 days
1	8.456	14.57	23.58
2	7.561	13.99	21.22
3	7.689	12.80	18.56
4	7.337	10.29	16.89
5	6.258	12.33	16.99
6	6.654	11.25	15.50
7	5.775	10.60	14.19
8	6.550	11.64	14.35
9	6.890	9.160	12.34
10	< LOD	< LOD	< LOD

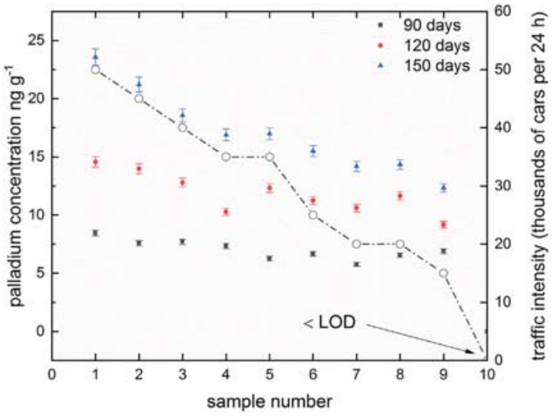

Fig. 3. Graphical representation of deposited Pd on lichens depending on exposure time and traffic intensity.

Lichens are considered to be very good bioindicators of metal pollution. However, the outliers in Fig. 4 may be caused by the metabolic processes occurring in the lichen (Hoffman, Rattner, Burton, Jr. and Cairns, Jr., 2003). In addition, the lichen's condition depends largely on weather conditions and overall environmental pollution. For longer monitoring, the bag technology is not conducive to the dangerous transition of the lichen to the latency phase under unsuitable conditions. This can occur in the case of insufficient moisture and may also be due to excessive contamination of the surface of the lichen insole. The cause of this is mainly airborne dust, black carbon, exhaust emissions, and metals (Zhao,

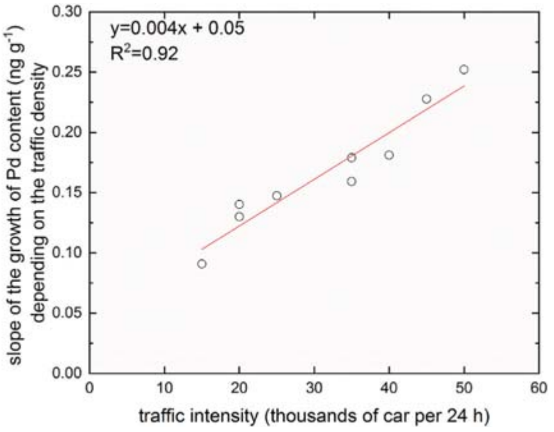

Fig. 4. Model curve for prediction of environmental load by palladium in dependence on density of automobile traffic.

Zhang, Jia, Liu, Chen, Li, Liu, Wu, Zhao and Liu, 2019). In addition, *Hypogymnia physodes* is the most widespread species of lichen in a temperate climate belt. It is one of the lichen species that is considered to be a nitrophobic organism. The nitrophobic species do not occur in nitrogen-enriched environments and avoid eutrophic sites. This fact may be another essential reason for the reduction of the metabolic functions of the exposed lichens because the exhaust gases to which the lichen became exposed to contain nitrogen oxides and nitrogen gas (Manninen, 2018).

4. Conclusions

A new preconcentration technique was developed for the determination of ultra-trace amounts of palladium in lichens. This preconcentration method has several advantages such as the height specificity and selectivity for Pd(II) sorption as a complex with dimethylglyoxime with a very high sorption efficiency (100%), a very low interference of matrix effect, a more affordable C18 silica gel sorbent, and the consumption of chemicals and organic solvents. In addition, the preconcentration efficacy of this method is good enough for the subsequent determination of Pd by using AAS or possibly other techniques with similar detection limits. Compared to commercially available sorbent QuadraSil™ TA, this approach appeared to be less prone to interferences with heavy metal ions and anions. For these reasons, the developed approach was used for determining Pd in lichens used as bioindicators of pollution caused by car traffic, which, as expected, increased with increasing exposition time and car traffic density.

The toxicity of Pd compounds has already been proven, but the environmental concentrations are still too low to draw conclusions on their direct effect on the health of humans living in areas with a high density of car traffic. For this reason, the amount of Pd and PGMs in various environmental objects should be continuously monitored. As a result of ever-increasing automotive traffic and exhaust emission requirements, the use of platinum-based catalysts will continue to be promoted and expanded. In the future, the palladium compound will be continuously emitted and thus endanger human health.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.113468.

References

Aničić, M., Tomašević, M., Tasić, M., Rajšić, S., Popović, A., Frontasyeva, M., Lierhagen, S., Steinnes, E., 2009. Monitoring of trace element atmospheric deposition using dry and wet moss bags: accumulation capacity versus exposure time: accumulation capacity versus exposure time. J. Hazard Mater. 171, 182–188. https://doi.org/10.1016/j.jhazmat.2009.05.112.

Bagheri, A., Taghizadeh, M., Behbahani, M., Akbar Asgharinezhad, A., Salarian, M., Dehghani, A., Ebrahimzadeh, H., Amini, M., 2012. Synthesis and characterization of magnetic metal-organic framework (MOF) as a novel sorbent, and its optimization by experimental design methodology for determination of palladium in environmental samples. Talanta 99, 132–139. https://doi.org/10.1016/j.talanta.2012.05.030.

Behbahani, M., Gorji, T., Mahyari, M., Salarian, M., Bagheri, A., Shaabani, A., 2014b. Application of polypropylene amine dendrimers (POPAM)-Grafted MWCNTs hybrid materials as a new sorbent for solid-phase extraction and trace determination of gold(III) and palladium(II) in food and environmental samples. Food Analytical Methods 7, 957–966. https://doi.org/10.1007/s12161-013-9698-1.

Behbahani, M., Najafi, F., Amini, M., Sadeghi, O., Bagheri, A., Hassanlou, P., 2014a. Solid phase extraction using nanoporous MCM-41 modified with 3,4-dihydroxybenzaldehyde for simultaneous preconcentration and removal of gold(III), palladium(II), copper(II) and silver(I). J. Ind. Eng. Chem. 20, 2248–2255. https://doi.org/10.1016/j.jiec.2013.09.057.

Conti, M., Cecchetti, G., 2001. Biological monitoring: lichens as bioindicators of air pollution assessment — a review: lichens as bioindicators of air pollution assessment — a review. Environ. Pollut. 114, 471–492. https://doi.org/10.1016/S0269-7491(00)00224-4.

Ek, K., Morrison, G., Rauch, S., 2004. Environmental routes for platinum group elements to biological materials—a review. Sci. Total Environ. 334–335, 21–38. https://doi.org/10.1016/j.scitotenv.2004.04.027.

Faurschou, A., 2011. Metal allergen of the 21st century-a review on exposure, epidemiology and clinical manifestations of palladium allergy. Contact Dermatitis 64, 185–195.

Garoufis, A., Hadjikakou, S., Hadjiliadis, N., 2009. Palladium coordination compounds as anti-viral, anti-fungal, anti-microbial and anti-tumor agents. Coord. Chem. Rev. 253, 1384–1397. https://doi.org/10.1016/j.ccr.2008.09.011.

Ghorbani-Kalhor, E., Behbahani, M., Abolhasani, J., 2015. Application of ion-imprinted polymer nanoparticles for selective trace determination of palladium ions in food and environmental samples with the aid of experimental design methodology. Food Analytical Methods 8, 1746–1757. https://doi.org/10.1007/s12161-014-0057-7.

Goncalves, A., Domínguez, J., Alvarado, J., 2008. Determination of Pd, Pt and Rh in vehicles escape fumes by GF-AAS and ICP-OES. Talanta 75, 523–527. https://doi.org/10.1016/j.talanta.2007.11.055.

Hoffman, D., Rattner, B., Burton Jr., G., Cairns Jr., J. (Eds.), 2003. Handbook of Ekotoxicology, second ed. Lewis Publishers, USA.

Huang, Y., Xiang, J., Wang, C., Ren, D., Johnson, David, Xu, T., 2019. Lichen as a biomonitor for vehicular emission of metals: a risk assessment of lichen consumption by the sichuan snub-nosed monkey (rhinopithecus roxellana): a risk assessment of lichen consumption by the sichuan snub-nosed monkey (rhinopithecus roxellana). Ecotoxicol. Environ. Saf. 180, 679–685. https://doi.org/10.1016/j.ecoenv.2019.05.047.

Johnson, Matthey, 2019. Johnson Matthey. http://www.platinum.matthey.com. (Accessed 2 September 2019).

Kielhorn, J., Melber, C., Keller, D., Mangelsdorf, I., 2002. Palladium — a review of exposure and effects to human health. Int. J. Hyg Environ. Health 205, 417–432. https://doi.org/10.1078/1438-4639-00180.

Kimuro, T., Gandhi, M., Kunda, U., Hamada, F., Yamada, M., 2017. Palladium(II) sorption of a diethylphosphate-modified thiacalix[6]arene immobilized on amberlite resin. Hydrometallurgy 171, 254–261. https://doi.org/10.1016/j.hydromet.2017.05.022.

Kłos, A., Ziembik, Z., Rajfur, M., Dołhańczuk-Śródka, A., Bochenek, Z., Bjerke, J., Tømmervik, H., Zagajewski, B., Ziółkowski, D., Jerz, D., Zielińska, M., Krems, P., Godyń, P., Marciniak, M., Świsłowski, P., 2018. Using moss and lichens in biomonitoring of heavy-metal contamination of forest areas in southern and north-eastern Poland. Sci. Total Environ. 627, 438–449. https://doi.org/10.1016/j.scitotenv.2018.01.211.

Komendova, R., Jezek, S., 2018. The distribution of platinum in the environment in large cities: a model study from Brno, Czech Republic. Int. J. Environ. Sci. Technol. https://doi.org/10.1007/s13762-018-1954-x.

Komendova, R., Nevrla, J., Kuta, J., Sommer, L., 2016. Innovative preconcentration technique ON polymer sorbent for simultaneous determination OF platinum group metals IN the waters and lichen hypogymnia physodes. Fresenius Environ. Bull. 25, 5172–5179.

Komendová, R., Žídek, J., Berka, M., Jemelková, M., Řezáčová, V., Conte, P., Kučerík, J., 2019. Small-sized platinum nanoparticles in soil organic matter: influence on water holding capacity, evaporation and structural rigidity: influence on water holding capacity, evaporation and structural rigidity. Sci. Total Environ. 694, 133822. https://doi.org/10.1016/j.scitotenv.2019.133822.

Komendova-Vlasankova, R., Sommer, L., 2002. Separation and preconcentration of platinum group metals and gold on modified silica and XAD sorbents in the presence of cationic surfactants for their determination by ICP-AES. Collect. Czechoslov. Chem. Commun. 67, 454–470. https://doi.org/10.1135/cccc20020454.

Kosarova, H., Komendova, R., Skeril, R., 2015. Development OF an analytical method for the determination OF platinum IN urban dust IN the agglomeration OF brno, Czech republic. Fresenius Environ. Bull. 24, 2070–2075.

Manninen, S., 2018. Deriving nitrogen critical levels and loads based on the responses of acidophytic lichen communities on boreal urban Pinus sylvestris trunks. Sci. Total Environ. 613–614, 751–762. https://doi.org/10.1016/j.scitotenv.2017.09.150.

Melber, C., Keller, D., Mangelsdorf, I., 2002. Environmental Health Criteria 226. http://www.inchem.org/documents/ehc/ehc/ehc226.htm. (Accessed 2 September 2019).

Moawed, E., 2006. Preparation of novel ion exchange polyurethane foam and its application for separation and determination of palladium in environmental samples. Anal. Chim. Acta 580, 263–270. https://doi.org/10.1016/j.aca.2006.07.072.

Nakajima, J., Ohno, M., Chikama, K., Seki, T., Oguma, K., 2009. Determination of traces of palladium in stream sediment and auto catalyst by FI-ICP-OES using on-line separation and preconcentration with QuadraSil TA. Talanta 79, 1050–1054. https://doi.org/10.1016/j.talanta.2009.02.035.

Panja, P., Bala, S., Pal, C., Ghosh, P., 1991. Infrared spectroscopic studies of dimethylglyoxime chelates of nickel, cobalt, copper, palladium and platinum. J. Mol. Struct. 249, 277–283. https://doi.org/10.1016/0022-2860(91)85073-C.

Pino, A., Alimonti, A., Conti, M., Bocca, B., 2010. Iridium, platinum and rhodium baseline concentration in lichens from Tierra del Fuego (South Patagonia, Argentina). J. Environ. Monit.: JEM 12, 1857–1863. https://doi.org/10.1039/c0em00097c.

Prichard, H., Fisher, P., 2012. Identification of platinum and palladium particles emitted from vehicles and dispersed into the surface environment. Environ. Sci. Technol. 46, 3149–3154.

Rauch, S., Hemond, H., Barbante, C., Owari, M., Morrison, G., Peucker-Ehrenbrink, B., Wass, U., 2005. Importance of automobile exhaust catalyst emissions for the deposition of Platinum, Palladium and Rhodium in the Northern hemisphere. Environ. Sci. Technol. 39, 8156–8162.

Ravindra, K., Bencs, L., Van Grieken, R., 2004. Platinum group elements in the environment and their health risk. Sci. Total Environ. 318, 1–43. https://doi.org/10.1016/S0048-9697(03)00372-3.

Reith, F., Campbell, S., Ball, A., Pring, A., Southam, G., 2014. Platinum in Earth surface environments. Earth Sci. Rev. 131, 1–21. https://doi.org/10.1016/j.earscirev.2014.01.003.

Road and Motorway Directorate of the Czech Republic. Traffic Census., n.d. Road and Motorway Directorate of the Czech Republic. Traffic census.

Rosner, G., Coenen-Stass, D., König, H., 1991. Environmental Health Criteria 125. http://www.inchem.org/documents/ehc/ehc/ehc125.htm. (Accessed 2 September 2019).

Sharififard, H., Soleimani, M., Ashtiani, F., 2012. Evaluation of activated carbon and bio-polymer modified activated carbon performance for palladium and platinum removal. J. Taiwan Inst. Chem. Eng.J. Taiwan Inst. Chem. Eng. 43, 696–703. https://doi.org/10.1016/j.jtice.2012.04.007.

Shrivastava, A., Gupta, V., 2011. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. Chronicles Young Sci. 21 https://doi.org/10.4103/2229-5186.79345.

Sutherland, R., 2007. Platinum-group element concentrations in BCR-723: a quantitative review of published analyses: a quantitative review of published analyses. Anal. Chim. Acta 582, 201–207. https://doi.org/10.1016/j.aca.2006.09.030.

Szczepaniak, K., Biziuk, M., 2003. Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution. Environ. Res. 93, 221–230. https://doi.org/10.1016/S0013-9351(03)00141-5.

Tokalıoğlu, Ş., Oymak, T., Kartal, Ş., 2004. Determination of palladium in various samples by atomic absorption spectrometry after preconcentration with dimethylglyoxime on silica gel. Anal. Chim. Acta 511, 255–260. https://doi.org/10.1016/j.aca.2004.02.015.

Twigg, M., 2011. Catalytic control of emissions from cars. Catal. Today 163, 33–41. https://doi.org/10.1016/j.cattod.2010.12.044.

Wiseman, C., Zereini, F., 2009. Airborne particulate matter, platinum group elements and human health: a review of recent evidence: a review of recent evidence. Sci. Total Environ. 407, 2493–2500. https://doi.org/10.1016/j.scitotenv.2008.12.057.

Zhao, L., Zhang, C., Jia, S., Liu, Q., Chen, Q., Li, X., Liu, X., Wu, Q., Zhao, L., Liu, H., 2019. Element bioaccumulation in lichens transplanted along two roads: the source and integration time of elements: the source and integration time of elements. Ecol. Indicat. 99, 101–107. https://doi.org/10.1016/j.ecolind.2018.12.020.

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Recent advances in the preconcentration and determination of platinum group metals in environmental and biological samples

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ABSTRACT

Platinum metals enter the environment primarily through the worldwide use of autocatalysts. The metals are released from the catalyst in the form of microparticles and nanoparticles, in elemental form, optionally in the form of surface-oxidized particles. Also important is the use of biologically active compounds of platinum group metals in oncological therapy, when they become the part of wastewaters. They move in all environmental compartments and are also subject to long-distance transport. However, they are still found in very low concentrations in the environment. Their direct determination is often difficult, using only highly sensitive analytical techniques. To use more common and more affordable techniques, a preconcentration step is necessary to increase their concentration to a measurable value. An overview of the application of preconcentration techniques and an overview of the current occurrence of platinum metals in individual matrices is presented.

1. Introduction

All platinum group metals (PGMs) (ruthenium, rhodium, palladium, osmium, iridium and platinum) occur naturally in the Earth's crust at very low concentrations. These metals, and their compounds, are very rare and their contents are in the order of tenths of ng.g-1 rock, with the exception of isolated deposits, where their concentration rises from 1000 to 10,000 times these values. They can be found, in their pure form, dispersed in river placers or bound as arsenides and sulphides in ores containing mainly Ni, Cu and Fe [1,2] Unlike other transition metals, PGMs are often found in their elemental form in natural sources with diffuse character.

PGMs are currently used in many modern technologies and products. Their consumption is steadily increasing (from 90 kt in 2010 to 106 kt in 2015). Their reserves and resources are mainly in South Africa [2,3]. They are "critical" metals because the demand for them can be influenced by the reliability of the supply, due to socio-economic reasons, but not in terms of the depletion of natural resources [4]. The current topic is the recycling of precious elements from electronic waste and used catalysts [5].

However, the anthropogenic entry of these metals and their compounds into the environment is alarming [6]. PGMs, especially platinum, palladium and rhodium, have become a significant source of the anthropogenic entry of heavy metals into the environment over the last three decades, due to their widespread use in the automotive industry. These elements are the main components of automotive catalytic converters and have a very important and irreplaceable function. They are involved in the elimination of toxic compounds produced by the combustion process. However, these elements are released when the car engine is running and become part of automotive emissions. In particular, the exhaust gas comprises a mixture of carbon monoxide, nitrogen oxides, hydrocarbons, as well as some incomplete combustion products, such as aldehydes, ketones, polycyclic aromatic hydrocarbons or carboxylic acids. PGMs reduce the content of these pollutants to concentration levels that meet the required emission standards. Since these standards are becoming increasingly stringent, the use of PGMs is currently essential. Other efforts have been made to reduce the formation of toxic fumes by engine modification, but catalytic systems have proven to be the most effective.

2. The fate of PGMs in the environment

Due to their low reactivity, low solubility and mobility, the natural cycle of these metals is very limited, but it is greatly impaired by the anthropogenic input of higher concentrations from automotive emissions. The emission of these metals and their

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Abbreviations

8HQS	8-hydroxyquinoline-5-sulfonic acid
AdCSV	adsorptive cathodic stripping voltammetry
Ajatine®	benzyldimethyl(dodecyl)ammonium bromide
APDC	ammoniumpyrrolidindithiocarbamate
AR	*aqua regia* (HCL:HNO_3 3:1)
Bond-Elut C18®	octadecylmodified silica gel
CMDCT	bis(carboxylmethyl)dithiocarbamate
CNF-PEI	cellulose nanofibrils modified with polyethyleneimine
CPC	1-hexadecylpyridinium chloride
CRM	certified reference material
CTAC	hexadecyl(trimethyl)ammonium chloride
DKTS APSG	diphenylketone-monothiosemicarbazone modified silica
DMG	dimethylglyoxime
DMG SG	dimethylglyoxime on silica
DPTH-gel	1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide
DPV	differential pulse voltammetry
ET-AAS	electrothermal atomic absorption spectrometry
F-AAS	flame atomic absorption spectrometry
HMImT	1-hexyl-3-methylimidazole-2-thione
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
IL	ionic liquids
LEP-OES	liquid electrode plasma optical emission spectrometry
Metalfix-Chelamin®	polymeric functionalised resin containing the tetraethylenepentamine group
MetaSep AnaLig®	selective sorbent for separation of Au, Pd, Pt from complex matrices
MW	microwave digestion
MWCNTs	multiwalled carbon nanotubes
NIES	National institute for environmental studies
NIST	National institute of standards and technology
PAMAM SG	amino-terminated dendrimer-like polyamidoamine immobilized silica gel
PAN-TU-GA	polyacrylonitrile sorbent modified with thiourea and glutaraldehyde
PAR	4-(2-pyridylazo) resorcinol
PEI/Al_2O_3	polyethylenimine modified alumina
PSTH	1,5-bis(2-pyridyl)-3-sulfophenyl methylene thiocarbonohydrazide
PSTH-cpg	1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide immobilized on an aminopropyl-controlled pore glass
QuadraSil™ TA	triamine modified silicagel
RF-OPT	Radio-frequency Oxygen Plasma treatment
RTILs	room temperature ionic liquids
SAX sorbent	mesoporous silica microparticles functionalized with quarternary amino groups
SBA-15	thiol-functionalized mesoporous silicas synthesized by co-condensation of tetraethoxysilane and mercaptopropyltriethoxysilane
Septonex®	(α-carbethoxypentadecyl)trimethylammonium bromide
SRM	standard reference material
Sterinol®	benzyl(dodecyl)dimethylammonium bromide
Strata C18-E®	octadecylmodified silica gel endcapped
Strata SDB-L®	styrene divinylbenzene sorbent
TTAB	trimethyl(tetradecyl)ammonium bromide
TU	thiourea
XAD-4®	polystyrene-divinylbenzene resin
Zephyramine®	benzyldimethyltetradecylammonium chloride

compounds is greatest in high-density traffic routes and the highest in places with poor dispersion conditions (tunnels, underpasses, etc.). However, this contamination has no local impact. Long-distance transport has been proven in the case of PGMs, especially platinum, confirming the global pollution of the entire planet [7].

A major risk of increasing concentrations of PGMs in individual environmental compartments is the inadequate and incomplete information on their toxicity, their effects on human health (and on individual organisms) and the effect of their bioaccumulation in the environment. The influence of platinum to human health and biological materials has been described in a few studies, e.g. Refs. [8–12], and [13]. Even the World Health Organization (WHO) does not have sufficient information about the behavior of these metals and their compounds in the environment, only partial information about platinum [14] and palladium [15]. The issue of platinum speciation and its impact on biological systems, toxicity and environmental behavior are very important. So far, however, there are very few works dealing with the platinum speciation [16,17]. The behavior and fate of rhodium and its compounds in the environment is almost unknown.

Other important sources of these metals in the environment are wastewater oncological treatment facilities [18,19]. PGMs, especially platinum compounds, but recently, also palladium [20,21] and rhodium, are in the form of some of their complex compounds potent cytostatics, i.e., antitumor metallopharmaceuticals. However, after an effective therapeutic response in the body, they are subsequently excreted from the patient. Contaminated waste water, which is often inefficiently cleaned in wastewater treatment plants, is becoming a point source of these metal compounds [22]. Their removal is only possible using special techniques [23]. These are present in soluble, bioavailable and biologically very active forms [24]. Very often, their cytostatic properties are accompanied by properties that are strongly toxic to living organisms, with a proven carcinogenic effect and very low biodegradability [25,26].

Therefore, anthropogenic inputs lead to the global contamination of all components of the environment. Priority inputs are car emissions and waste water. However, PGMs and their compounds penetrate into all living and nonliving components. They are found in airborne dust [27,28], road dust [29], soil [29–31], vegetation [32,33], wastewater [23,34], river water [24], aquatic organisms and sediments [35], the bodies of animals at higher levels of the food chain [36] and even in the human body [37,38].

3. Preconcentration of PGMs

PGMs, despite the above-mentioned anthropogenic sources, are found in environmental components at very low concentrations. Often, such low concentrations cannot be determined directly, even using the most sensitive analytical techniques with very low detection limits (LOD) and quantification limits (LOQ). These techniques include, in particular, the inductively coupled plasma mass spectrometry (ICP-MS) [2]. Buying and operating these devices is often very expensive, evaluated by comparing the cost of acquisition and the cost of one analysis [39]. Therefore, sorption techniques have often been studied, developed, tested and innovated to enrich low levels of PGMs to reach values that can be measured by more common and less expensive techniques, such as electrothermal atomic absorption spectrometry (ET-AAS), flame atomic absorption spectrometry (F-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and liquid electrode plasma optical emission spectrometry (LEP-OES). However, these techniques require the use of a preconcentration step (see comparison of typical limits of detection [40] of the above techniques in Table 1).

The most effective method of concentrating PGMs is the Solid Phase Extraction (SPE) method. There are a number of sorbents, whether conventional, selective or specific, which are used for this purpose. The advantage of this technique is not only that it increases the concentration of selected elements to measurable values, but also their simultaneous separation from the sample matrix, which often interferes with the determination of the analyte [42].

Very important parameters for the testing and selection of suitable sorbents are not only their selectivity, specificity, sorption and elution efficiency, and the possibility of reuse, but also price, market availability, the consumption of chemicals and organic solvents used in the sorption process, the effect of possible interference on the sorption course, usability in analyzing real samples and the amount and type of generated chemical waste. The economic and ecological aspect of the developed method of determining PGMs also plays an important role.

The mechanism of platinum sorption largely depends on the type of sorbent and can take place through various physicochemical interactions, such as adsorption on the surface of the sorbent, sorption of the analyte in the form of chelate, binding of the resulting ion pair, ion associate, or mechanism of ion exchange [43]. By choosing a suitable sorbent with a high affinity for the analyte, it is possible to achieve an effective sorption with high selectivity. Selective and specific reactions with selected organic agents, or substances forming agents, can be used.

In the adsorption mechanism, the analyte is bound on the solid phase by van der Waals forces or hydrophobic interactions. These hydrophobic interactions are particularly useful in highly non-polar sorbents. The most common sorbents of this type are silica gel, modified by hydrocarbon chain, or selected organic functional groups. Another large group is polymeric styrene-divinylbenzene copolymer sorbents. Elution, in this case, is carried out with organic solvents such as methanol, ethanol or acetonitrile. However, PGMs are most commonly found in solution in the form of their halogenocomplexes, so direct sorption to this type of sorbent does not take place. The ionic forms of PGMs must react with a suitable organic reagent and the resulting complex is then bound to the sorbent only by hydrophobic interactions, or the sorbent must be modified with the selected organic reagent.

The formation of an analyte chelate with a suitable organic chelating agent that contains a heteroatom in its molecule can be used for selective sorption. Nitrogen heteroatoms (nitro-, amino-, imido- and azo-) and sulfur (most commonly thio-functional groups) have a significant affinity for PGMs. The most important requirements for efficient and highly effective sorption are the selectivity of the agent, the stability of the chelate formed, sufficiently rapid chelate kinetics, the good solubility of the chelate formed and the sufficiently strong binding of the resulting chelate to the sorbent surface [42].

Table 1
Typical detection limits of PGMs, calculated at 3 σ [40,41].

Element	Method/LOD				
	F-AAS	ET-AAS	ICP-OES	LEP-OES	ICP-MS
	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$ng\ L^{-1}$
Ir	500	4	4	–	0.01–0.1
Os	100	–	5	–	0.01–0.1
Pd	10	0.5	2	3	0.01–0.1
Pt	75	4.5	20	57	0.01–0.1
Rh	3	0.4	5	–	0.01–0.1
Ru	100	0.75	4	–	0.01–0.1

If we modify the non-polar sorbent with an ion-pairing agent, it binds with its non-polar part to the non-polar sorbent by hydrophobic forces. With its polar part, it forms an ion pair with the analyte ions, or complexes, in solution. Typical examples of ion-pairing agents are quaternary ammonium salts and alkyl sulfates.

In ion-exchange sorption, sorbents containing anionic or cationic functional groups are used. These groups may be attached to silica gel or styrene-divinylbenzene copolymer-type sorbents. The ion exchange then occurs between the analyzed solution and the solid sorbent. The ion exchange groups can be strongly or weakly dissociated and the applicability depends on the pH value. Strongly dissociated groups are useful throughout the pH range, while the weakly dissociated groups were only useful at a pH higher than the pKa (dissociation constant). Strongly cationic exchange groups include sulfone groups and strongly anionic-exchange quaternary ammonium salts. The weak cation exchangers are the carboxyl groups and the weak anion exchangers are ternary amines.

A very interesting issue in the area of preconcentration of PGMs in recent years is the use of microextraction. The reason is to minimize the use of organic reagents and to replace them with more environmentally friendly alternatives. These include ionic liquids, also called 21st century solvents [44]. Ionic liquids (ILs) are those substances that consist of an organic cation and an inorganic or organic anion and have a melting point below 100 C. The most interesting are ionic liquids already at room temperature (RTILs). The main advantages of ILs are zero vapor pressure, thermostability, excellent solvation properties, non-flammability and low toxicity. ILs play a key role in microextraction analytical techniques used to preconcentration of PGMs from environmental and biological samples. 1-Hexyl-3-methylimidazole-2-thione [45] or 1-alkyl-3-methylimidazolium chloride [46] was used as an ionic liquid for microextraction of PGMs.

Significant attention was paid to PGMs in the late 1990s. The reason for this was the introduction of a platinum-containing automotive catalytic converter into the compulsory equipment of each car. This was the primary reason for the development of new analytical procedures for the determination of ultra-trace concentrations of these metals. Consequently, the preconcentration techniques solved the fundamental problem of these analytes in real samples and raised their concentration to a measurable level. A very detailed review of the preconcentration techniques used to determine trace amounts of PGMs presents works [47]. There are described hydrophobic sorbents with surface immobilized complexing or chelating agents, complexing and chelating sorbents, fiber complexing sorbents, liquid anion exchange sorbents and extraction agents, as well as basic anion exchange sorbents.

Table 2 clearly shows the possible SPE platinum metal techniques in the coming years. Types of sorbents, sorption techniques, analytes, sorption conditions, end detection techniques and the usability for analysis of real samples are all mentioned. A very important part of the analytical determination of PGMs in environmental and biological samples is also the sample preparation step and its decomposition. In the case of water samples, the sample is only filtered through a membrane filter of predefined pore size and acidified before analysis, most often with hydrochloric acid. Acidic solution is very important in trace analysis of

Table 2
Overview of preconcentration techniques used for determination of PGMs.

Sorbent	Analyte	Eluent	Detection technique	Type of sample	Sample treatment	LOD	Ref.
Modified hydrophobic sorbents							
CMDCT on XAD-4®	Pd, Pt, Rh	5 mol L^{-1} NH_3	ICP-OES	beans, tobacco	high pressure asher in AR	μg L^{-1} Pd 0.03 Pt 0.1 Rh 0.01	[49]
Metalfix-Chelamin®	Pt, Pd	0.5 mol L^{-1} TU in 12 mol L^{-1} HCl	ICP-OES	complex matrices, CRM NIST	muffle furnace with Na_2O_2, dissolution in AR	μg L^{-1} Pt 0.022 Pd 0.0025	[50]
PAN-TU-GA	Pt, Pd	0.5 mol L^{-1} TU in 0.5 mol L^{-1} HCl	FTIR, X-ray	leaching solutions, spent catalyst, electric wastes, spent plating solutions	NiS fire-leaching	–	[51]
Strata SDB-L® modif.: APDC, TU, PAR, 8HQS, Zephyramine®, Septonex®, Ajatine®	Pt, Pd, Rh, Ru, Os, Ir	acetonitrile:HCl 4:1	ICP-MS	lichen, spiked river water, spiked peat bog water	MW in AR	ng L^{-1} Ru 0.0184 Rh 0.0025 Pd 0.1177 Os 0.0387 Ir 0.0092 Pt 0.0084	[52]
MetaSep AnaLig®	Pd, Pt	1:0.5 TU:HCl	LEP-OES	waste plating waters, complex waste matrices	without any pre-processing	μg L^{-1} Pd 3.1 Pt 57.3	[41]
Modified silicagel							
Separon® SGX C18 - Septonex	Pt, Pd, Rh, Ru, Os, Ir	ethanol	ICP-OES ICP-MS	CRM NIES 8, engine soot, airborne particulates	low pressure RF-OPT MW in HNO_3 and H_2O_2	–	[53]
Separon® SGX C18 Separon® SGX RPS Separon®SGXphenyl modif.: Septonex®, Sterinol®,TTAB, CTAC, CPC	Pt, Pd, Rh, Ru, Os, Ir	ethanol methanol propan-2-ol acetone acetonitrile	ICP-OES	spiked samples: soil, power station dust, natural waters	MW in AR	μg L^{-1} Ir 7.3 Os 1.9 Pd 6.6 Pt 5.3 Rh 6.2 Ru 3.5	[54]
DPTH-gel	Pt	2 mol L^{-1} HNO_3	ET-AAS	catalyst, vegetation, soil, water	MW in HCl, HNO_3, H_2O_2	μg L^{-1} Pt 0.8	[55]
DMG SG	Pd	1 mol L^{-1} HCl in acetone	FAAS ET-AAS	street dust, anode slime, catalytic converters, rock sample	evaporation in AR to dryness	μg L^{-1} Pt 90 μg L^{-1} Pt 10	[56]
DPTH-gel	Pd	4 mol L^{-1} HCl	ET-AAS	CRM NIST lentil, bovine liver, vegetation	MW in AR MW in HNO_3, H_2O_2	μg L^{-1} Pd 0.4	[57]
PAMAM SG	Pd	0.2% TU	F-AAS	nickel alloy, anode slime	Na_2CO_3, Na_2O_2, dissolution in AR	μg L^{-1} Pd 3.9	[58]
DKTS APSG	Pd	TU in HCl	F-AAS	catalytic converter, spiked tap water	evaporation in AR to dryness	μg L^{-1} Pd 5	[59]
Bond-Elut C18®/Septonex® Strata C18-E®/Septonex®	Pt	acetonitrile	ET-AAS	airborne urban dust	MW in AR	μg L^{-1} Pt 1.137	[27]
SAX sorbent	Pt, Pd	2 mol L^{-1} in 1.2 mol L^{-1} HCl	ICP-MS	CRM BCR 723, road dust	MW in HNO_3, H_2O_2, HCl, HF	ng/g Pt 2 Pd 1	[60]
SBA-15	Pt	TU	ET-AAS	platinum ore CRM SARM 7, geological samples	MW in HNO_3	–	[61]
Bond-Elut C18®/Septonex®	Pt, Pd	acetonitrile	ET-AAS	lichen, moss, needle	boiling under reflux in AR	μg L^{-1} Pt 2.627 Pd 2.282	[32]
				soil, tunnel dust	MW in AR	μg L^{-1} Pt 1.14	[29]

SBA-15	Pd	0.6 mol l^{-1} TU	ET-AAS	soil, road dust	MW in AR	µg L^{-1} Pd 0.048	[62]
Bond-Elut C18®/DMG QuadraSil™ TA	Pd	1 mol L^{-1} in ethanol 0.05 mol L^{-1} TU	ET-AAS	lichen	boiling under reflux in AR	µg L^{-1} Pd 1.110	[63]
Anion exchangers							
Amberlite® IRA-68 Amberlite® IRA-93 Amberlite® IRA-400	Pt, Pd, Rh	4 mol l^{-1} HCl	ICP-OES	catalytic converters	leaching in HCl, $NaClO_3$	–	[64]
Dowex® 1-X8	Pt, Pd, Rh, Ir, Ru	0.3 mol L^{-1} TU in 0.1 mol L^{-1} HCl	ICP-OES	synthetic PGMs solution	–	µg L^{-1} Ru 14 Rh 11 Pd 13 Ir 9 Pt 29	[65]
			ICP-MS			µg L^{-1} Ru 0.22 Rh 0.03 Pd 0.17 Ir 0.07 Pt 0.11	
Dowex® 1-X10	Pt	0.1 mol L^{-1} TU v 0.1 mol L^{-1} HCl	ICP-OES	road dust	heating in AR	µg L^{-1} Pt 15 Pd 19	[66]
PSTH Dowex® 1-X8	Pt	2 mol L^{-1} HNO_3	ET-AAS	catalyst, CRM NIST 2557, soil	MW in AR	µg L^{-1} Pt 1	[67]
				vegetation	MW in HNO_3, H_2O_2		
				natural water	–		
PSTH Dowex® 1-X8	Pt	2 mol L^{-1} HNO_3	ICP-OES	CRM NIST 2557 spiked waters	MW in acids –	µg L^{-1} Pt 7.4	[68]
Bio-RadAG®MP-1M Bio-Rad AG® 1-X8 Bio-Rad AG® 1-X2	Pt, Rh	0.1 mol L^{-1} TU	ICP-OES	chloride solution	–	–	[69]
PSTH-cpg	Pt, Pd, Ir	0.03% TU in 3.2% HNO_3	ICP-MS	CRM NIST 2557, spiked sediments, spiked natural waters	MW in AR	µg L^{-1} Pt 0.0785 Pd 0.0555 Ir 0.0001	[70]
XUS 43600.00 Lewatit M + MP600 Purolite S985	Pt, Pd, Rh	1 mol L^{-1} TU in 2 mol L^{-1} HCl	ICP-OES	chloride solutions from leached from the catalyst	–	–	[71]
Rossion-1p Rossion-5 Rossion-10	Pt, Pd, Rh, Ru, Ir	–	ICP-OES	compound solutions	–	–	[72]
Dowex® 50W-X8	Pt, Pd	0.5 mol L^{-1} HCl	ICP-OES	soil, vegetation	boiling under reflux in AR	µg L^{-1} Pt 12.24 Pd 13.78	[73]
			ET-AAS			µg L^{-1} Pt 1.131 Pd 2.210	
Dowex®1-X8 (50–100) Dowex®1-X8 (200–400) Dowex®1-X10 (50–100)	Pt, Pd	0.5 mol L^{-1} HCl 1 mol L^{-1} HCl	ET-AAS	soil	boiling under reflux in AR	µg L^{-1} Pt 1.669 Pd 3.208	[74]

(continued on next page)

Table 2 (*continued*)

Sorbent	Analyte	Eluent	Detection technique	Type of sample	Sample treatment	LOD	Ref.
Cation Exchangers							
Bio-Rad AG® 50W-X8	Ru, Rh, Pd,Ir, Pt	0.5 mol L^{-1} HCl	ICP-MS	geological materials	MW in AR, HF alkali fusion method Na_2O_2, Na_2CO_3	μg L^{-1} Ru 0.20 Rh 0.03 Pd 0.16 Ir 0.07 Pt 0.11	[75]
Dowex® 50W-X8	Pt, Pd, Rh	0.6 mol L^{-1} HCl	ICP-MS	road dust, roadside soil BCR 723, infiltration basin, wetland sediments	MW in AR	ng L^{-1} Pt 0.01 Pd 0.72 Rh 0.05	[76] [77]
Dowex® 50W-X8 Dowex® 50W-X12	Pt, Pd	–	ET-AAS	soil	boiling under reflux in AR	μg L^{-1} Pt 1.669 Pd 3.208	[74]
Special Sorbents							
MWCNTs	Pd	0.4 mol L^{-1} TU	F-AAS	standard samples, road dust, wastewater	evaporation in AR to dryness	μg L^{-1} Pd 0.3	[78]
PEI/Al_2O_3	Pd	1 mol L^{-1} TU in 1 mol L^{-1} HCl	ET-AAS	spiked solutions, spiked sea water	–	ng L^{-1} Pd 2	[79]
CNF-PEI	Pt	–	ICP-OES	solutions from leached from the catalyst	–	–	[80]

PGMs. It ensures the presence of PGMs in the form of soluble chlorocomplexes and prevents sorption on the walls of the containers in which the sample is stored. Solid environmental samples are usually decomposed in *aqua regia* by microwave decomposition, heating and evaporation to near dryness or boiling under reflux. In the case of PGMs, the fire assay method can also be used for decomposition [48]. The sample preparation procedures are given in both Table 2 and 3.

4. Monitoring of PGMs in the environment

Compared to other elements, PGMs are naturally found in the environment in very low concentrations, often in elemental form, and their occurrence is diffuse in nature. All PGMs always occur together. Palladium and platinum are present in the content of 0.015−0.010 mg.kg-1, Ru, Os, Rh and Ir in lower concentrations of 0.005−0.0001 mg.kg-1. They naturally occur either in pure form, dispersed in alluvial placer deposits, or bound in ores in the form of arsenides and sulfides, along with other more common metals such as nickel, copper and iron. The largest deposits are found in South Africa, Russia and North America.

Although these metals are naturally rare, since the end of the 20th century their content in the environment has been steadily increasing due to human anthropogenic activity. They are used extensively in transport, industry and medicine. These are the main routes of entry into the environment for these metals and their compounds.

PGMs are used primarily for their excellent catalytic properties and are predominantly applied in industry as catalysts. Palladium is used in hydrogenation and dehydrogenation reactions, platinum as a catalyst in nitric acid production, petroleum reforming and especially both platinum and palladium in automotive catalysts. Other PGMs are used to increase the hardness of various alloys and in catalytic and hydrogenation reactions, but their greater industrial use is limited by their rarity and high cost. In recent years, the use of palladium has increased, partially replacing platinum in automotive catalysts. This is due to its availability and lower price, which has now risen because of its increased use (see Fig. 1).

Platinum-based catalysts have been used in nitric acid production for about a century. Modern nitric acid production processes consist of three steps. The first step is the oxidation of ammonia gas with air to form nitric oxide, to achieve high conversion efficiency on the platinum-rhodium catalyst. Rhodium is added to reduce platinum losses. The nitric oxide is cooled and further oxidized to nitrogen dioxide, which is then absorbed in water to form nitric acid. Platinum and rhodium losses can be as high as 300 mg per ton of nitric acid. The end use of nitric acid is in the production of nitrogen fertilizers, an important source of plant nutrients. In this way, platinum also enters the environment and the loss of platinum from catalysts is several tons a year worldwide.

Fig. 2 shows the massive use of platinum and palladium in the production of automotive catalysts. Platinum was used for this purpose in 2018, about 95 t, but palladium already 270 t and rhodium only about 27 t. Over time, more and more precious metals are recycled. In 2018, almost 65 t of platinum, 100 t of palladium and about 11 t of rhodium were recycled from the used autocatalysts. Recycled automotive catalysts can contain up to 2000 g.t-1 platinum, which is a significantly higher quantity than is found in the ores from which it is extracted. These high levels of platinum in waste make it, economically, very interesting when compared to the economic side of ore mining.

Road transport is the largest source of platinum metal pollution. There are studies that estimate up to a 40% release of PGMs from catalysts into the environment during the first 100,000 km travelled by a car [81]. PGMs emissions have been proven, both by

Table 3
Overview of PGMs concentration in selected environmental and biological objects.

Matrix	Country	Analyte/concentration	Detection technique	Sample treatment	LOD	Ref.
Air (pg m^{-3})						
	Brno, Czech Republic	Pt 2.3–51.5	ET-AAS	MW in AR	µg L^{-1} Pt 1.137	[27]
	Zagreb, Croatia	Pt 0.488–1.071 Pd 3.856–5.600 Rh 0.444–0.750	ICP-MS	MW in HNO_3, HCl	pg m^{-3} Pt 0.045 Pd 0.908 Rh 0.177	[28]
	Munich, Germany	Pt 62.00–21.50	DPV	MW	pg m^{-3} Pt 0.5	[87]
Water (pmol L^{-1})						
Rain water River water Sea water	Tokyo Bay, Otsuchi Bay, Japan	Pt 0.12–0.62 Pt 0.07–6.51 Pt 0.29–7.74	ICP-MS	0.45 µm membrane filter	pmol kg^{-1} Pt 0.18	[24]
Sea water	–	(fg g^{-1}) Pt 0.1–100	–	–	–	[88]
Sea water	Atlantic Ocean	Pt 0.11–0.32	AdCSV	< 0.2 µm cartridge, UV digestion	pmol L^{-1} Pt 0.026	[89]
Sediment (ng g^{-1})						
	Mediterranean Coast	Pt 6.0–15.0	AdCSV	evaporation in HCl, HNO_3 to dryness	ng g^{-1} Pt 0.03	[35]
	Perth, Australia wetland sediments	Pt 9.0–103.8 Pd 5.4–61.2 Rh 1.5–17.2	ICP-MS	MW in AR	ng L^{-1} Pt 0.01 Pd 0.72 Rh 0.05	[77]
	Gironde Estruary, France	(pmol g^{-1}) Pt 1.0–7.0	AdCSV	evaporation in HCl, HNO_3 to dryness	pmol g^{-1} Pt 0.11	[90]
	Tagus Estruary and Prodelta, Portugal	Pt 9.5	AdCSV	evaporation in HCl, HNO_3 to dryness	ng g^{-1} Pt 0.05	[91]
	Brno, Czech Republic	Pt 8.839–48.82 Pd 1.800–7.674	ET-AAS	boiling under reflux in AR	µg L^{-1} Pt 7.290 Pd 1.119	[92]
Soil (ng g^{-1})						
	Brno, Czech Republic	Pt 10.5–15.7	ET-AAS	MW in AR	µg L^{-1} Pt 1.14	[29]
	Palermo, Italy	Pt 0.6–2210	AdCSV	MW in HNO_3, dissolution in AR	LOQ 0.3 ng g^{-1}	[30]
	Berlin, Germany (1992–2013)	Pt 1.28–4.05 Pd 0.305–1.69 Rh 0.0450–0.330	ICP-MS	MW in AR	–	[31]
	Toronto, Canada	Pt 59 Pd 98 Rh 9.6	ICP-MS	MW in HNO_3, HCl	ng L^{-1} Pd 4.4 Pt 7.5 Rh 9.0	[93]
Dust (ng g^{-1})						
Air dust	Brno, Czech Republic	Pt 61.9–2997.7	ET-AAS	MW in AR	µg L^{-1} Pt 1.137	[27]
Tunnel dust	Brno, Czech Republic	Pt 66.3–192	ET-AAS	MW in AR	µg L^{-1} Pt 1.14	[29]
Road dust	Toronto, Canada	Pt 26-69 Pd 10-121 Rh 7.8–15	ICP-MS	MW in HNO_3, HCl	ng L^{-1} Pd 4.4 Pt 7.5 Rh 9.0	[93]
Biological samples (ng g^{-1})						
Tree bark	urban areas rural areas	Pt 12.9 5.5	ICP-MS	Acid digestion	ng L^{-1} Pt 0.8	[94]
Grass	Brno, Czech Republic	Pt 10.0–11.6	ET-AAS	MW in AR	µg L^{-1} Pt 1.14	[29]
Lichen Moss Needles	Brno, Czech Republic	Pt <LOD-23.18 Pd 5.140–47.08 Pt <LOD-59.40 Pd 2.979–8.449 Pt <LOD-7.278 Pd 3.017–12.09	ET-AAS	boiling under reflux in AR	µg L^{-1} Pt 2.627 Pd 2.282	[32]
Mussels	Mediterranean Coast	Pt 0.09–0.66	ICP-MS	digestion in HCl, HNO_3	ng g^{-1} Pt 0.003	[35]
Wild oysters	Gironde Estruary, France	(pmol g^{-1}) 0.80–3.1	AdCSV	evaporation in AR to dryness	pmol g^{-1} Pt 0.44	[90]
Clams	Brno, Czech Republic	Pt 11.71–21.68 Pd 2.886–5.395	ET-AAS	boiling under reflux in AR	µg L^{-1} Pt 7.290 Pd 1.119	[92]
Human sample (ng g^{-1})						
Urine	Germany human habitants of urban areas		DPV (Pt)	UV photolysis		[38]
	rural areas	Pt 3.43				

(*continued on next page*)

Table 3 (*continued*)

Matrix	Country	Analyte/concentration	Detection technique	Sample treatment	LOD	Ref.
	working in urban areas living next to highly frequented roads	Pt 2.06			ng L^{-1} Pt 0.2	
		Pt 3.27 Rh 7.27	ICP-MS (Rh)	MW	ng L^{-1} Rh 0.3	
Urine	Munich, Germany	Pt 6.5–20		DPV	UV photolysis in H_2O_2 and H_2SO_4	ng L^{-1} Pt 1
[87]						
Blood	Croatia Czech Republic Poland Slovakia Slovenia Sweden	(ng L^{-1}) Pt 0.6–5.2 Pd 5–9,0.3 Rh 0.4–3.6	ICP-MS	leaching in HNO_3, HCl	ng L^{-1} Pt 0.6 Pd 1-5 Rh 0.4	[95]

testing the emission gases in laboratories and by determining their presence in environmental compartments. This release from the catalyst is due to the chemical and physical processes taking place on the catalytic surface. They are released due to mechanical abrasion, a high operating temperature and ongoing oxidation-reduction reactions. The release is further influenced by a number of factors, such as speed and driving style, start-stop driving, operating temperature, fuel type and quality, the age of the catalytic converter and, in particular, the engine type. The diesel engine produces significantly higher emissions than the gasoline engine with a three-way catalytic converter. Depending on these conditions, emissions can range from ng to μg PGMs per 1 km of driving, representing their contents in contaminated air around busy roads at pg.m-3 [27]. However, the exact amount of platinum released cannot be predicted, given the abundance of factors and research over 30 years.

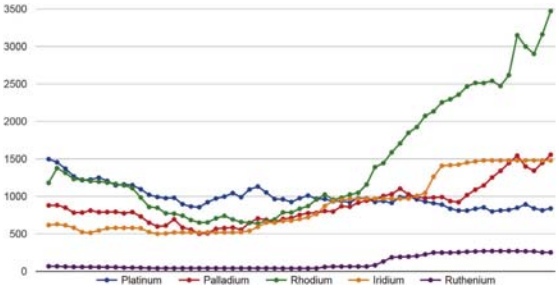

Fig. 1. Average monthly prices (x-axis months, y-axis \$/oz, 1 oz - 31.1035 g) of PGMs in 2014–2019 Ref. [3].

The PGMs emitted are most often in the form of metal nanoparticles, which can be adsorbed onto the catalyst support (Al2O3) or exhaust gas (soot) particles. These particles become part of the polluted atmosphere and, depending on their size, are deposited at different distances from the source of pollution, depending on the density of car traffic, meteorological conditions and terrain morphologies. They adhere to dust, surface soil and vegetation around roads and, under certain conditions, may also be subject to long-distance transport. This is evidenced by the finding of increased concentrations of PGMs in snow and ice in European mountain areas and in Greenland, with a significant increase in the 1990s [81]. The advantage of analyzing different layers of ice is the chronological information that can indicate the time of contamination.

Another important source of PGMs emissions is medicine. Platinum-based drugs, especially cisplatin, *cis*-diaminodichloro Pt (II), and carboplatin, *cis*- (diamine-1,1-cyclobutane-1,1-dicarboxylato) Pt (II), have been widely used as effective cytostatics since the early 1970s. The principle of the anti-tumor effect of cisplatin is to inhibit DNA synthesis by forming cross-links in and between DNA strands. In addition to inhibiting DNA synthesis, cisplatin has immunosuppressive, radio sensitizing and antibacterial properties. It is used to treat a wide range of cancers: bronchogenic carcinoma, testicular carcinoma, ovarian carcinoma, cervical carcinoma, endometrium, prostate, bladder, melanoma, sarcomas, ENT tumors, brain epithelial carcinoma and malignant lymphomas [82]. In contrast to its therapeutic effects, cisplatin has

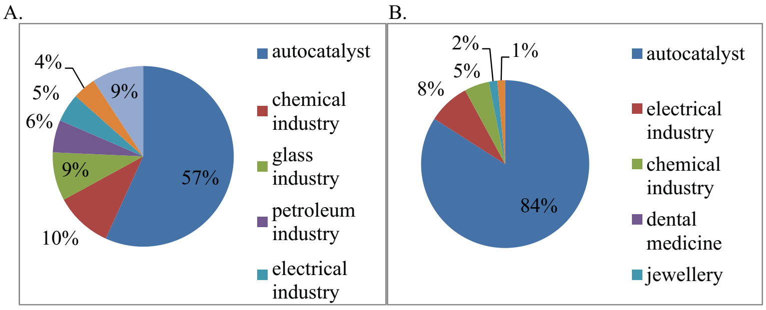

Fig. 2. Use of A. platinum and B. palladium in 2018, according to Ref. [3].

a number of negative effects on the treated patient. When used, cisplatin has nephrotoxic, neuropathic, ototoxic effects, allergic manifestations and is suspected of having a possible carcinogenicity and many other undesirable side effects. The excretion of cisplatin, as well as other platinum metallopharmaceuticals, takes place exclusively in urine and bile. In the first five days, 27–43% of cisplatin is excreted. In this way, platinum gets into the waste water, not only of treatment facilities, but also of households after the patients leave home. Its concentrations are in ng.l-1 [22].

The main problem with the occurrence of platinum drugs in wastewater is the presence of platinum in a soluble, bioavailable and highly toxic form, as opposed to the more inert metallic forms of platinum emitted by automobile catalysts. However, it may be partially present in the form of surface oxidized particles. These are more easily subjected to complex reactions and produce bioavailable forms of platinum, most often in the form of chlorocomplexes or complexes with organic ligands. The most common ligands complexing platinum are phosphates (from phosphate fertilizers), chlorides (from road surface maintenance in the winter months), citrates (produced by plant roots) and fulvic acids (produced by natural decomposition of organic matter) [83]. So far, there is very little relevant information on the bioavailability of PGMs, their ecotoxicity and environmental fate.

An important parameter is the mobility of platinum compounds in individual environmental compartments. This is clearly dependent on the form of PGMs, the pH of the soils, the redox potential and the presence of the above complexing agents. It is estimated that about 10% of the platinum emitted from autocatalysts is water soluble under environmental conditions. For palladium and rhodium, a solubility of even 50% is expected [11], as well as higher bioavailability. It was experimentally determined in the order of $Pd > Pt \geq Rh$, when the transformation coefficient (ratio of metal concentrations in the plant and in the soil from which the plant grows) was tested. Therefore, palladium is the most soluble, mobile and bioavailable of all PGMs. The highest concentrations were found in plant roots where binding to sulfur-containing substances, in animal bodily fluids and in bird feathers [84].

Blood proteins play a decisive role in the transport of PGMs in animal bodies. Up to 80% of platinum in the blood is found in erythrocytes. The stability of protein binding depends on the type of compound. Elevated concentrations were detected in the kidneys and liver, where they bind to metallothionenins (proteins with cysteine). These proteins have a high affinity for all heavy metals (Cd, Cu, Hg, etc.) and their formation is indicated by the presence of these risk elements. The presence of Pt (II) induces the formation of metallothioneines and binds them up to 100 times faster than other heavy metals, so they can be displaced. Relevant information on the behavior of other PGMs and their compounds is not yet known. Similarly, there is no known information on the biotransformation reactions of PGMs by the formation of methyl compounds. Only laboratory studies have been conducted and there is no direct evidence of methylation of PGMs in environmental compartments.

The environmental toxicity of PGMs is clearly dependent on their size (in the case of emitted particles), their form and the compounds in which they occur. In elemental metal form they are inert, but in the form of nanoparticles their toxicity increases due to dissolution, oxidation and complexing reactions, under both biotic and abiotic conditions. Platinum nanoparticles may enter into different parts of the plant [85] and can also affect local physicochemical processes in the soil [86]. From WHO materials [14,15], providing data only for platinum and palladium, there is a risk of particulate inhalation and allergic properties. Pd (II) is even the most common sensitizer of all metals. The greatest risk lies, primarily, for people living in polluted areas with chronic exposure to them. At present, they have been found in large urban agglomerations contents of PGMs in all parts of the environment. Their quantity is growing steadily and strongly depends on the density of automobile traffic. Therefore, the inhabitants of these areas make up the most vulnerable population [13,29,32,81], and [84].

The analysis of the individual components of the environment can be done in several ways. When analyzing the polluted atmosphere, samples of solid particles of airborne dust are collected by trapping on glass fiber filters using an automatic sampler, by sucking the polluted air. These filters are then analyzed and the analyte concentration in the atmosphere can be determined from the volume of sieved air during sampling, most often in units of pg.m-3 for PGMs. Using 24-h sampling, the analyte can be concentrated on the filter to a measurable value. When interpreting the results and drawing conclusions, it is necessary to take into account the sampling conditions (season, sampling time - working days, weekends, traffic intensity, meteorological conditions, etc.).

The most easily analyzable matrix is water and aqueous solutions. A disadvantage in the analysis of environmental water samples is the very low content of PGMs, which are in units of ng.l-1. In this case, it is necessary to use preconcentration techniques to enrich the analyte to a measurable concentration value. It is thus possible to increase the analyte content in the analyzed sample by one order, with respect to the used end detection instrumental analytical technique.

Sediment analysis is very closely related to the analysis of natural water. For a complete overview of the behavior of PGMs in water, an interesting analyte is sediment taken from the same location as the water sample. However, complications and losses of the analyte may occur when sediment is sampled. When assessing the platinum content of sediments, one should take note of the possible inhomogeneity of sediment samples and the influence of local conditions (the presence of other pollutants, flow behavior at the sampling site, climatic and meteorological conditions, etc.).

Very often, the analyzed material is the soil around busy roads. When collecting the soil, a number of factors should be taken into account: distance of the sampling site from the potential source of contamination (from the road), depth of sampling, traffic intensity at the site, local conditions (the presence of vegetation, barriers, etc.), climatic conditions and meteorological conditions.

Road dust is also an important matrix for assessing the state of environmental pollution from automobile traffic. Its sampling is more demanding and safety rules for sampling must be observed, especially when it comes to tunnel dust sampling. This matrix has the highest content of PGMs, as confirmed by the data in Table 3.

For a comprehensive overview of the distribution of PGMs in environmental components, it is also necessary to determine their content in biological matrices, so-called bioindicators. For this purpose, there is an effective tool: biomonitoring. By means of biomonitoring, it is possible to find relationships between the pollution of individual components of the environment (air, aquatic and terrestrial ecosystems) and organisms living within it. Possible adverse effects on human health can also be predicted from biomonitoring data.

A bioindicator is an organism that indicates the environmental pollution by selected pollutants. Plant bioindicators are most commonly used and are divided into sensitive, accumulative and test bioindicators. In the case of the biomonitoring of PGMs, accumulation bioindicators, with the ability to accumulate pollutants from environmental components, are used. These substances accumulate in the body without causing visible damage and their uptake depends on their concentration in the environment. These bioindicators can be analyzed immediately after collection - passive bioindications, or using active (exposure) bioindications. Selected plant species are deliberately exposed to the polluted environment and react by accumulating pollutants (accumulative indicator). Bioindicators that are easily and available year-round include mosses, lichens and pine needles. These bioindicators have the advantage of being evergreen and can be sampled throughout the year. In addition, mosses and lichens have a large surface area that is not covered with a cuticle. This allows for the uptake of pollutants from the atmosphere almost exclusively by the particle deposition process. Furthermore, grass vegetation samples are often analyzed, together with soil analysis, for platinum metal content. Sampling conditions for biological samples should also be taken into account. In particular, season, climatic and meteorological conditions, type of sample, and distance from the source of contamination.

A current overview of the occurrence of PGMs in the environment, indicating the location and analytical detection techniques, is shown in Table 3.

5. Conclusion

It is clear from the above that PGMs affect us all. The issues stemming from their use are global, whether in terms of resources, their use in industry, applications, automotive use, waste and wastewater management and environmental contamination, not only from a local, but also from a global perspective. Emission limits from automotive sources are getting steadily tighter throughout the world and the necessary use of PGMs to reduce emissions contributes to an upward trend in global platinum, palladium and rhodium levels.

The most commonly used method for the determination of PGMs is the ICP-MS technique, providing highly sensitive simultaneous multi-elementary ability. Trace values of PGMs can also be determined by atomic absorption and emission techniques, ET-AAS and ICP-OES. Voltammetric methods also show high sensitivity. Trace concentrations of PGMs in environmental and biological samples often require appropriate methods and procedures for separation and preconcentration prior to their analytical determination. The preconcentration of PGMs therefore includes especially innovative or newly developed sorption techniques mentioned in this work. Modified hydrophobic sorbents, which include in particular modified silica gel and anion exchange sorbents, are most commonly used. Sorbents of the nanotubes and nanofibers type, often modified to increase the sorption selectivity of PGMs, are also newly used. When analyzing using the preconcentration technique, it is always necessary to take into account all relevant factors, such as the sample type, the method of sample decomposition, the matrix effect, using eluent and the end detection technique with required detection limit. Preconcentration techniques can be used to increase the concentration of PGMs to a value measurable by more common analytical techniques such as ET-AAS and ICP-OES.

There are many other challenges in determining ultra-trace concentrations of PGMs, given their presence in the environment in the form of nanoparticles, and the fact that the oxidation state, speciation, and the form of occurrence significantly affect the reactivity, bioavailability and toxic properties of PGMs.

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References

[1] F. Reith, S. Campbell, A. Ball, A. Pring, G. Southam, Platinum in Earth surface environments, Earth Sci. Rev. 131 (2014) 1–21. https://doi.org/10.1016/j.earscirev.2014.01.003.

[2] C. Rao, G. Reddi, Platinum group metals (PGM); occurrence, use and recent trends in their determination, Trac. Trends Anal. Chem. 19 (2000) 565–586. https://doi.org/10.1016/S0165-9936(00)00031-5.

[3] Matthey Johnson. http://www.platinum.matthey.com, 2019. (Accessed 18 October 2019).

[4] G. Mudd, S. Jowitt, T. Werner, Global platinum group element resources, reserves and mining – a critical assessment, Sci. Total Environ. 622–623 (2018) 614–625. https://doi.org/10.1016/j.scitotenv.2017.11.350.

[5] Y. Ding, S. Zhang, B. Liu, H. Zheng, C. Chang, C. Ekberg, Recovery of precious metals from electronic waste and spent catalysts: a review: a review, Resour. Conserv. Recycl. 141 (2019) 284–298. https://doi.org/10.1016/j.resconrec.2018.10.041.

[6] L. Bencs, K. Ravindra, R. Van Grieken, Platinum: environmental pollution and health effects, Elsevier, Burlington, 2011, pp. 580–595. https://doi.org/10.1016/B978-0-444-52272-6.00602-4.

[7] S. Rauch, H. Hemond, C. Barbante, M. Owari, G. Morrison, B. Peucker-Ehrenbrink, U. Wass, Importance of automobile exhaust catalyst emissions for the deposition of Platinum, Palladium and Rhodium in the Northern hemisphere, Environ. Sci. Technol. 39 (2005) 8156–8162.

[8] J. Kielhorn, C. Melber, D. Keller, I. Mangelsdorf, Palladium – a review of exposure and effects to human health, Int. J. Hyg Environ. Health 205 (2002) 417–432. https://doi.org/10.1078/1438-4639-00180.

[9] K. Ek, G. Morrison, S. Rauch, Environmental routes for platinum group elements to biological materials—a review, Sci. Total Environ. 334–335 (2004a) 21–38. https://doi.org/10.1016/j.scitotenv.2004.04.027.

[10] K. Ravindra, L. Bencs, R. Van Grieken, Platinum group elements in the environment and their health risk, Sci. Total Environ. 318 (2004) 1–43. https://doi.org/10.1016/S0048-9697(03)00372-3.

[11] C. Wiseman, F. Zereini, Airborne particulate matter, platinum group elements and human health: a review of recent evidence: a review of recent evidence, Sci. Total Environ. 407 (2009) 2493–2500. https://doi.org/10.1016/j.scitotenv.2008.12.057.

[12] F. Annesofie, M. Torkil, J. D, T. P, Metal allergen of the 21st century—a review on exposure, epidemiology and clinical manifestations of palladium allergy, Contact Dermatitis 64 (2011) 185–195. https://doi.org/10.1111/j.1600-0536.2011.01878.x.

[13] J. Pawlak, E. Łodyga-Chruścińska, J. Chrustowicz, Fate of platinum metals in the environment, J. Trace Elem. Med. Biol. 28 (2014) 247–254. https://doi.org/10.1016/j.jtemb.2014.03.005.

[14] G. Rosner, D. Coenen-Stass, H. König, Environmental health criteria 125 (1991). http://www.inchem.org/documents/ehc/ehc/ehc125.htm. (Accessed 8 March 2018).

[15] C. Melber, D. Keller, I. Mangelsdorf, Environmental health criteria 226 (2002). http://www.inchem.org/documents/ehc/ehc/ehc226.htm. (Accessed 25 February 2019).

[16] C. Ojeda, F. Rojas, J. Pavón, Determination of platinum by graphite furnace atomic absorption spectrometry in foods and beverages using an automated on-line separation-preconcentration system, Food Control 17 (2006) 365–369. https://doi.org/10.1016/j.foodcont.2005.01.002.

[17] W. Mortada, M. Hassanien, A. El-Asmy, Speciation of platinum in blood plasma and urine by micelle-mediated extraction and graphite furnace atomic absorption spectrometry, J. Trace Elem. Med. Biol. 27 (2013) 267–272. https://doi.org/10.1016/j.jtemb.2013.04.004.

[18] N. Vyas, A. Turner, G. Sewell, Platinum-based anticancer drugs in waste waters of a major UK hospital and predicted concentrations in recipient surface waters, Sci. Total Environ. 493 (2014) 324–329. https://doi.org/10.1016/j.scitotenv.2014.05.127.

[19] A. Turner, L. Mascorda, Particle–water interactions of platinum-based anticancer drugs in river water and estuarine water, Chemosphere 119 (2015) 415–422. https://doi.org/10.1016/j.chemosphere.2014.06.074.

[20] A. Garoufis, S. Hadjikakou, N. Hadjiliadis, Palladium coordination compounds as anti-viral, anti-fungal, anti-microbial and anti-tumor agents, Coord. Chem. Rev. 253 (2009) 1384–1397. https://doi.org/10.1016/j.ccr.2008.09.011.

[21] B. Mavroidi, M. Sagnou, K. Stamatakis, M. Paravatou-Petsotas, M. Pelecanou, C. Methenitis, Palladium(II) and platinum(II) complexes of derivatives of 2-(4′-aminophenyl)benzothiazole as potential anticancer agents, Inorg. Chim. Acta 444 (2016) 63–75. https://doi.org/10.1016/j.ica.2016.01.012.

[22] J. Vidmar, A. Martinčič, R. Milačič, J. Ščančar, Speciation of cisplatin in environmental water samples by hydrophilic interaction liquid chromatography coupled to inductively coupled plasma mass spectrometry, Talanta 138 (2015) 1–7. https://doi.org/10.1016/j.talanta.2015.02.008.

[23] K. Lenz, G. Koellensperger, S. Hann, N. Weissenbacher, S. Mahnik, M. Fuerhacker, Fate of cancerostatic platinum compounds in biological wastewater treatment of hospital effluents, Chemosphere 69 (2007) 1765–1774. https://doi.org/10.1016/j.chemosphere.2007.05.062.

[24] A. Mashio, H. Obata, H. Tazoe, M. Tsutsumi, A. Ferrer i Santos, T. Gamo, Dissolved platinum in rainwater, river water and seawater around Tokyo Bay and Otsuchi Bay in Japan, Estuarine, Estuar. Coast Shelf Sci. 180 (2016) 160–167. https://doi.org/10.1016/j.ecss.2016.07.002.

[25] M. Chen, S. Chen, M. Du, S. Tang, M. Chen, W. Wang, H. Yang, Q. Chen, J. Chen, Toxic effect of palladium on embryonic development of zebrafish, Aquat. Toxicol. 159 (2015) 208–216. https://doi.org/10.1016/j.aquatox.2014.12.015.

[26] S. Zimmermann, C. Wolff, B. Sures, Toxicity of platinum, palladium and rhodium to Daphnia magna in single and binary metal exposure experiments,

Environ. Pollut. 224 (2017) 368–376. https://doi.org/10.1016/j.envpol.2017.02.016.

[27] H. Kosarova, R. Komendova, R. Skeril, Development of an analytical method for the determination of platinum in urban dust in the agglomeration of Brno, Czech Republic, Fresenius Environ. Bull. 24 (2015) 2070–2075. Go to ISI://WOS:000371185200010.

[28] J. Rinkovec, G. Pehnec, R. Godec, S. Davila, I. Bešlić, Spatial and temporal distribution of platinum, palladium and rhodium in Zagreb air, Sci. Total Environ. 636 (2018) 456–463. https://doi.org/10.1016/j.scitotenv.2018.04.295.

[29] R. Komendova, S. Jezek, The distribution of platinum in the environment in large cities: a model study from Brno, Czech Republic, Int. J. Environ. Sci. Technol. 16 (2019) 3109–3116. https://doi.org/10.1007/s13762-018-1954-x.

[30] S. Orecchio, D. Amorello, Platinum levels in urban soils from Palermo (Italy); Analytical method using voltammetry, Microchem. J. 99 (2011) 283–288. https://doi.org/10.1016/j.microc.2011.05.016.

[31] M. Birke, U. Rauch, J. Stummeyer, H. Lorenz, B. Keilert, A review of platinum group element (PGE) geochemistry and a study of the changes of PGE contents in the topsoil of Berlin, Germany, between 1992 and 2013, J. Geochem. Explor. 187 (2018) 72–96. https://doi.org/10.1016/j.gexplo.2017.09.005.

[32] R. Komendova, The use of bioindicators for assessing atmospheric pollution with platinum metals, Fresenius Environ. Bull. 5A (2018) 3444–3451.

[33] H. Gawrońska, A. Przybysz, E. Szalacha, K. Pawlak, K. Brama, A. Miszczak, M. Stankiewicz-Kosyl, S. Gawroński, Platinum uptake, distribution and toxicity in Arabidopsis thaliana L. plants, Ecotoxicol. Environ. Saf. 147 (2018) 982–989. https://doi.org/10.1016/j.ecoenv.2017.09.065.

[34] K. Kümmerer, E. Helmers, P. Hubner, G. Mascart, M. Milandri, F. Reinthaler, M. Zwakenberg, European hospitals as a source for platinum in the environment in comparison with other sources, Sci. Total Environ. 225 (1999) 155–165. https://doi.org/10.1016/S0048-9697(98)00341-6.

[35] M. Abdou, J. Schäfer, R. Hu, T. Gil-Díaz, C. Garnier, C. Brach-Papa, J. Chiffoleau, S. Charmasson, F. Giner, L. Dutruch, G. Blanc, Platinum in sediments and mussels from the northwestern Mediterranean coast: temporal and spatial aspects: temporal and spatial aspects, Chemosphere 215 (2019) 783–792. https://doi.org/10.1016/j.chemosphere.2018.10.011.

[36] K. Ek, S. Rauch, G. Morrison, P. Lindberg, Platinum group elements in raptor eggs, faeces, blood, liver and kidney, Sci. Total Environ. 334–335 (2004b) 149–159. https://doi.org/10.1016/j.scitotenv.2004.04.067.

[37] Y. Wang, X. Li, Health risk of platinum group elements from automobile catalysts, Procedia Eng. 45 (2012) 1004–1009. https://doi.org/10.1016/j.proeng.2012.08.273.

[38] S. Munker, S. Kilo, C. Röß, P. Jeitner, R. Schierl, T. Göen, H. Drexler, Exposure of the German general population to platinum and rhodium – Urinary levels and determining factors, Int. J. Hyg Environ. Health 219 (2016) 801–810. https://doi.org/10.1016/j.ijheh.2016.07.019.

[39] R. Thomas, Practical Guide to ICP-MS, 1 ed., CRC Press, New York, 2008. http://algol.fis.uc.pt/jap/ICP-MS-Primer-Thomas.pdf. (Accessed 17 October 2019).

[40] AAS, GFAAS, ICP or ICP-MS? Which technique should I use?, 1 ed., Thermo Elemental, United Kingdom, 2001. http://oliver.chemistry.ucsc.edu/122/Lab5%20Handout.pdf. (Accessed 17 October 2019).

[41] S. Barua, I. Rahman, M. Miyaguchi, A. Mashio, T. Maki, H. Hasegawa, On-site analysis of gold, palladium, or platinum in acidic aqueous matrix using liquid electrode plasma-optical emission spectrometry combined with ion-selective preconcentration, Sens. Actuators B Chem. 272 (2018) 91–99. https://doi.org/10.1016/j.snb.2018.05.132.

[42] V. Camel, Solid phase extraction of trace elements, Spectrochim. Acta B At. Spectrosc. 58 (2003) 1177–1233. https://doi.org/10.1016/S0584-8547(03)00072-7.

[43] V. Camel, Solid-phase extraction, in: Sample Preparation for Trace Element Analysis, Elsevier (2003) 393–457. https://doi.org/10.1016/S0166-526X(03)41014-3.

[44] R. Marcinkowska, K. Konieczna, Ł. Marcinkowski, J. Namieśnik, A. Kloskowski, Application of ionic liquids in microextraction techniques: current trends and future perspectives: current trends and future perspectives, Trac. Trends Anal. Chem. 119 (2019) 115614. https://doi.org/10.1016/j.trac.2019.07.025.

[45] X. Yin, H. Yi, Q. Wang, Y. Wang, X. Sun, C. Lv, J. Guo, Y. Yang, Extraction and separation of multiple platinum group metals from hydrochloric acid solution with sole 1-hexyl-3-methylimidazole-2-thione using microextraction method, Hydrometallurgy 174 (2017) 167–174. https://doi.org/10.1016/j.hydromet.2017.10.009.

[46] Y. Tong, C. Wang, Y. Huang, Y. Yang, Extraction and stripping of platinum from hydrochloric acid medium by mixed imidazolium ionic liquids, Ind. Eng. Chem. Res. 54 (2015) 705–711. https://doi.org/10.1021/ie503502g.

[47] R. Vlasankova, L. Sommer, Solid phase extraction and preconcentration for the determination of trace amounts of platinum group metals in environmental and biotic material - a critical review, Chem. Pap. Slovak Acad. Sci. 53 (1999) 200–209.

[48] J. Barakso, Determination of the Precious Metals: Selected Instrumental Methods: J.C. Van Loon and R.R. Barefoot. Wiley, New York, 1991, 276 pp, US$ 115.00: Selected Instrumental Methods, J. Geochem. Explor. 43 (1992) 294–295. https://doi.org/10.1016/0375-6742(92)90114-N.

[49] M. Lee, G. Tölg, E. Beinrohr, P. Tschöpel, Preconcentration of palladium, platinum and rhodium by on-line sorbent extraction for graphite furnace atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry, Anal. Chim. Acta 272 (1993) 193–203. https://doi.org/10.1016/0003-2670(93)80569-7.

[50] M. Muzikar, C. Fontàs, M. Hidalgo, J. Havel, V. Salvadó, A preconcentration system using polyamine Metalfix-Chelamine resin for the on-line determination of palladium(II) and platinum(IV) by inductively coupled plasma optical emission spectrometry, Talanta 70 (2006) 1081–1086. https://doi.org/10.1016/j.talanta.2006.02.021.

[51] M. Morcali, B. Zeytuncu, Investigation of adsorption parameters for platinum and palladium onto a modified polyacrylonitrile-based sorbent, Int. J. Miner. Process. 137 (2015) 52–58. https://doi.org/10.1016/j.minpro.2015.02.011.

[52] R. Komendova, J. Nevrla, J. Kuta, L. Sommer, Innovative preconcentration technique on polymer sorbent for simultaneous determination of platinum group metals in the waters and lichen Hypogymnia Physodes, Fresenius Environ. Bull. 25 (2016) 5172–5179. ISI://WOS:000391345600011.

[53] R. Vlasankova, V. Otruba, J. Bendl, M. Fisera, V. Kanicky, Preconcentration of platinum group metals on modified silicagel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates, Talanta 48 (1999) 839–846. https://doi.org/10.1016/S0039-9140(98)00100-3.

[54] R. Komendova-Vlasankova, L. Sommer, Separation and preconcentration of platinum group metals and gold on modified silica and XAD sorbents in the presence of cationic surfactants for their determination by ICP-AES, Collect. Czechoslov. Chem. Commun. 67 (2002) 454–470. https://doi.org/10.1135/cccc20020454.

[55] C. Bosch Ojeda, F. Sánchez Rojas, J. Cano Pavón, A. Garcıa de Torres, Automated on-line separation–preconcentration system for platinum determination by electrothermal atomic absorption spectrometry, Anal. Chim. Acta 494 (2003) 97–103. https://doi.org/10.1016/S0003-2670(03)01014-6.

[56] Ş. Tokalıoğlu, T. Oymak, Ş. Kartal, Determination of palladium in various samples by atomic absorption spectrometry after preconcentration with dimethylglyoxime on silica gel, Anal. Chim. Acta 511 (2004) 255–260. https://doi.org/10.1016/j.aca.2004.02.015.

[57] F. Rojas, C. Ojeda, J. Pavón, Automated on-line separation preconcentration system for palladium determination by graphite furnace atomic absorption spectrometry and its application to palladium determination in environmental and food samples, Talanta 70 (2006) 979–983. https://doi.org/10.1016/j.talanta.2006.05.048.

[58] X. Wu, P. Liu, Q. Pu, Q. Sun, Z. Su, Preparation of dendrimer-like polyamidoamine immobilized silica gel and its application to online preconcentration and separation palladium prior to FAAS determination, Talanta 62 (2004) 918–923. https://doi.org/10.1016/j.talanta.2003.10.011.

[59] R. Sharma, A. Pandey, S. Gulati, A. Adholeya, An optimized procedure for preconcentration, determination and on-line recovery of palladium using highly selective diphenyldiketone-monothiosemicarbazone modified silica gel, J. Hazard Mater. 209–210 (2012) 285–292. https://doi.org/10.1016/j.jhazmat.2012.01.022.

[60] W. Nischkauer, M. Neouze, F. Vanhaecke, A. Limbeck, Extraction and preconcentration of platinum and palladium from microwave-digested road dust via ion exchanging mesoporous silica microparticles prior to their quantification by quadrupole ICP-MS, Mikrochim. Acta 182 (2015) 2369–2376. https://doi.org/10.1007/s00604-015-1643-0.

[61] M. Barczak, J. Dobrzyńska, M. Oszust, E. Skwarek, J. Ostrowski, E. Zięba, P. Borowski, R. Dobrowolski, Synthesis and application of thiolated mesoporous silicas for sorption, preconcentration and determination of platinum, Mater. Chem. Phys. 181 (2016) 126–135. https://doi.org/10.1016/j.matchemphys.2016.06.042.

[62] J. Dobrzyńska, R. Dobrowolski, R. Olchowski, E. Zięba, M. Barczak, Palladium adsorption and preconcentration onto thiol- and amine-functionalized mesoporous silicas with respect to analytical applications, Microporous Mesoporous Mater. 274 (2019) 127–137. https://doi.org/10.1016/j.micromeso.2018.07.038.

[63] R. Komendova, The HR-CS-GF-AAS determination and preconcentration of palladium in contaminated urban areas, especially in lichens, Environ. Pollut. (2019) 113468. https://doi.org/10.1016/j.envpol.2019.113468.

[64] R. Gaita, S. Al-Bazi, An ion-exchange method for selective separation of palladium, platinum and rhodium from solutions obtained by leaching automotive catalytic converters, Talanta 42 (1995) 249–255. https://doi.org/10.1016/0039-9140(94)00246-O.

[65] I. Jarvis, M. Totland, K. Jarvis, Assessment of Dowex 1-X8-based anion-exchange procedures for the separation and determination of ruthenium, rhodium, palladium, iridium, platinum and gold in geological samples by inductively coupled plasma mass spectrometry, Analyst 122 (1997b) 19–26. https://doi.org/10.1039/a606169i.

[66] P. Kovacheva, R. Djingova, Ion-exchange method for separation and concentration of platinum and palladium for analysis of environmental samples by inductively coupled plasma atomic emission spectrometry, Anal. Chim. Acta 464 (2002) 7–13. https://doi.org/10.1016/S0003-2670(02)00428-2.

[67] M. González García, F. Sánchez Rojas, C. Bosch Ojeda, A. García de Torres, J. Cano Pavón, On-line ion-exchange preconcentration and determination of traces of platinum by electrothermal atomic absorption spectrometry, Anal. Bioanal. Chem. 375 (2003) 1229–1233. https://doi.org/10.1007/s00216-002-1679-y.

[68] N. Martos, P. Rudner, A. de Torres, J. Pavón, Development of an FI-ICP method for on-line preconcentration and determination of platinum, Microchimica Acta 148 (2004) 35–42. https://doi.org/10.1007/s00604-004-0256-9.

[69] P. Sun, J. Lee, M. Lee, Separation of platinum(IV) and rhodium(III) from acidic chloride solution by ion exchange with anion resins, Hydrometallurgy 113–114 (2012) 200–204. https://doi.org/10.1016/j.hydromet.2011.12.009.

[70] M. Alonso Castillo, A. García de Torres, E. Vereda Alonso, M. Siles Cordero, J. Cano Pavón, Multi-element determination of Pt, Pd and Ir traces in environmental samples by ICP-MS after pre-concentration, Talanta 99 (2012) 853–858. https://doi.org/10.1016/j.talanta.2012.07.042.

[71] A. Nikoloski, K. Ang, D. Li, Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins, Hydrometallurgy 152 (2015) 20–32. https://doi.org/10.1016/j.hydromet.2014.12.006.

[72] A. Miroshnichenko, Sorption recovery of platinum metals from compound solutions, Procedia Eng. 152 (2016) 8–12. https://doi.org/10.1016/j.proeng.2016.07.607.

[73] S. Ježek, Stanovení Platinových Kovů Ve Velkých Městských Aglomeracích, Diplomová Práce, 2016.

[74] J. Sýkora, Využití Iontoměničů Pro Prekoncentraci Platinových Kovů, Diplomová práce, 2017.

[75] I. Jarvis, M. Totland, K. Jarvis, Determination of the platinum-group elements in geological materials by ICP-MS using microwave digestion, alkali fusion and cation-exchange chromatography, Chem. Geol. 143 (1997a) 27–42. https://doi.org/10.1016/S0009-2541(97)00098-3.

[76] J. Whiteley, F. Murray, Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia, Sci. Total Environ. 317 (2003) 121–135. https://doi.org/10.1016/S0048-9697(03)00359-0.

[77] J. Whiteley, F. Murray, Autocatalyst-derived platinum, palladium and rhodium (PGE) in infiltration basin and wetland sediments receiving urban runoff, Sci. Total Environ. 341 (2005) 199–209. https://doi.org/10.1016/j.scitotenv.2004.09.030.

[78] D. Afzali, R. Jamshidi, S. Ghaseminezhad, Z. Afzali, Preconcentration procedure trace amounts of palladium using modified multiwalled carbon nanotubes sorbent prior to flame atomic absorption spectrometry: 1st Nano update, Arabian. J. Chem 5 (2012) 461–466. https://doi.org/10.1016/j.arabjc.2011.01.017.

[79] M. Taher, Z. Daliri, H. Fazelirad, Simultaneous extraction and preconcentration of copper, silver and palladium with modified alumina and their determination by electrothermal atomic absorption spectrometry, Chin. Chem. Lett. 25 (2014) 649–654. https://doi.org/10.1016/j.cclet.2013.12.025.

[80] H. Hong, H. Yu, M. Park, H. Jeong, Recovery of platinum from waste effluent using polyethyleneimine-modified nanocelluloses: effects of the cellulose source and type: effects of the cellulose source and type, Carbohydr. Polym. 210 (2019) 167–174. https://doi.org/10.1016/j.carbpol.2019.01.079.

[81] C. Wiseman, F. Zereini (Editors), Platinum Metals in the Environment, 1 ed., Springer, Berlin, 2015.

[82] Cisplatina (n.d.), www.sukl.cz.

[83] O. Šebek, M. Mihaljevič, L. Strnad, V. Ettler, J. Ježek, R. Štědrý, P. Drahota, L. Ackerman, V. Adamec, Dissolution kinetics of Pd and Pt from automobile catalysts by naturally occurring complexing agents, J. Hazard Mater. 198 (2011) 331–339. https://doi.org/10.1016/j.jhazmat.2011.10.051.

[84] F. Zereini, F. Alt (Editors), Palladium Emissions in the Environment, 1 ed., Springer, Berlin, 2005.

[85] E. Kranjc, D. Mazej, M. Regvar, D. Drobne, M. Remškar, Foliar surface free energy affects platinum nanoparticle adhesion, uptake, and translocation from leaves to roots in arugula and escarole, Environ. Sci.: Nano 5 (2018) 520–532. https://doi.org/10.1039/C7EN00887B.

[86] R. Komendová, J. Žídek, M. Berka, M. Jemelková, V. Řezáčová, P. Conte, J. Kučerík, Small-sized platinum nanoparticles in soil organic matter: influence on water holding capacity, evaporation and structural rigidity: influence on water holding capacity, evaporation and structural rigidity, Sci. Total Environ. 694 (2019) 133822. https://doi.org/10.1016/j.scitotenv.2019.133822.

[87] R. Schierl, Environmental monitoring of platinum in air and urine, Microchem. J. 67 (2000) 245–248. https://doi.org/10.1016/S0026-265X(00)00068-0.

[88] M. Sharma, Platinum Group Elements and Their Isotopes in the Ocean, Academic Press, Oxford, 2019, pp. 174–180. https://doi.org/10.1016/B978-0-12-409548-9.11556-8.

[89] D. López-Sánchez, A. Cobelo-García, M. Rijkenberg, L. Gerringa, H. de Baar, New insights on the dissolved platinum behavior in the Atlantic Ocean, Chem. Geol. 511 (2019) 204–211. https://doi.org/10.1016/j.chemgeo.2019.01.003.

[90] M. Abdou, J. Schäfer, A. Cobelo-García, P. Neira, J. Petit, D. Auger, J. Chiffoleau, G. Blanc, Past and present platinum contamination of a major European fluvial–estuarine system: insights from river sediments and estuarine oysters: insights from river sediments and estuarine oysters, Mar. Chem. 185 (2016) 104–110. https://doi.org/10.1016/j.marchem.2016.01.006.

[91] A. Cobelo-García, P. Neira, M. Mil-Homens, M. Caetano, Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal), Mar. Pollut. Bull. 62 (2011) 646–650. https://doi.org/10.1016/j.marpolbul.2010.12.018.

[92] M. Novotný, Studium Kontaminace Říčních Sedimentů Platinovými Kovy, Diplomová práce, 2018.

[93] C. Wiseman, Z. Hassan Pour, F. Zereini, Platinum group element and cerium concentrations in roadside environments in Toronto, Canada, Chemosphere 145 (2016) 61–67. https://doi.org/10.1016/j.chemosphere.2015.11.056.

[94] R. Ma, I. Staton, C. McLeod, M. Gomez, M. Gomez, M. Palacios, Assessment of airborne platinum contamination via ICP-mass spectrometric analysis of tree bark, J. Anal. At. Spectrom. 16 (2001) 1070–1075. https://doi.org/10.1039/b102940c.

[95] G. Rentschler, I. Rodushkin, M. Cerna, C. Chen, F. Harari, R. Harari, M. Horvat, F. Hruba, L. Kasparova, K. Koppova, A. Krskova, M. Krsnik, J. Laamech, Y. Li, L. Löfmark, T. Lundh, N. Lundström, B. Lyoussi, D. Mazej, J. Osredkar, K. Pawlas, N. Pawlas, A. Prokopowicz, S. Skerfving, J. Snoj Tratnik, V. Spevackova, Z. Spiric, A. Sundkvist, U. Strömberg, D. Vadla, K. Wranova, S. Zizi, I. Bergdahl, Platinum, palladium, rhodium, molybdenum and strontium in blood of urban women in nine countries, Int. J. Hyg Environ. Health 221 (2018) 223–230. https://doi.org/10.1016/j.ijheh.2017.10.017.

Příloha 11

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Small-sized platinum nanoparticles in soil organic matter: Influence on water holding capacity, evaporation and structural rigidity

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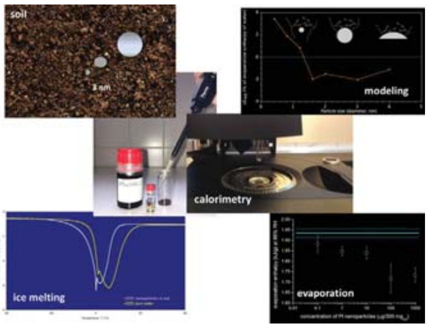
HIGHLIGHTS

- Pt nanoparticles influence physico-chemical properties of pure water.
- Different effects on water fractions in soil organic matter were observed.
- The structural rigidity of soil organic matter is increased by nanoparticles.
- Some effects were observed at environmentally relevant concentrations.
- Higher content of nanoparticles increased the aliphatic crystallites content.

GRAPHICAL ABSTRACT



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ABSTRACT

Engineered and anthropogenic nanoparticles represent a new type of pollutants. Up until now, many studies have reported its adverse effect on biota, but the potential influence on the properties and functions of environmental compartments has largely been ignored. In this work, the effect of Pt nanoparticles on the functions and properties of model soil organic matter has been studied. Using differential scanning calorimetry and molecular modeling, the effect of a wide range of 3 nm Pt nanoparticles concentrations on water holding capacity, the strength of water binding, the stability of water molecule bridges and the content of aliphatic crystallites was studied. It was found that strong hydration of the nanoparticles influences the 3D water structural network and acts as kosmotropic agents (structure-forming) in water bridges and as chaotropic agents (i.e. water destructuring) in larger water volumes. Contrarily, the interaction with soil organic matter moieties partially eliminates these effects. As a result, the 3 nm Pt nanoparticles decreased the evaporation enthalpy of water in soil organic matter and supported soil desiccation. They also increased the strength of water molecule bridges and increased the soil structural rigidity even at low concentrations. Additionally, at high concentrations, they decreased the water content in soil organic matter and induced the aliphatic moieties' crystallization. It is concluded that the small-sized Pt nanoparticles, and perhaps other types as well, may affect the local physicochemical processes in soils and may consequently contribute to enhanced evapotranspiration and deterioration of soil functions.

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1. Introduction

The use of new materials and technologies generates new types of pollution. Nowadays, one of the most discussed issues is the unintentional release of engineered (produced for industrial and environmental applications) and anthropogenic (formed as by-products during biomass burning, fossil fuel combustion and waste incineration) nanoparticles (Bundschuh et al., 2018). The most used engineered nanoparticles are carbon nanotubes, fullerenes, and zero-valent iron/nickel while the most frequent anthropogenic ones are soot, black carbon, and vehicle exhaust emissions (Rajput et al., 2017). The amount of nanoparticles emitted to the environment is steadily increasing (Pulit-Prociak and Banach, 2016), thereby attracting interest because of their potential risk to living organisms and human health (Xing et al., 2016).

Both natural and anthropogenic/engineered nanoparticles occur in soils. According to Navrotsky (2003a), the soil is a very complex mixture of different types of nanomaterials, where the forms of transport occur from nanoscale to macroscale dimension. The naturally occurring nanoparticles, i.e. clay minerals, metal (hydr)oxides, and humic substances (Theng and Yuan, 2008) are not present as discrete entities, but mostly as clusters. The fate of anthropogenic/engineered nanoparticles entering soils depends on the reactivity, mobility, bioavailability and interactions with their surroundings (Bakshi et al., 2015), but the awareness of their effect on soil properties is still poor due to lack of assessment methods, their fast agglomeration and mostly unknown amount of emitted particles (Xing et al., 2016). Therefore, available literature mainly reports information on the types of engineered nanoparticles in the environment, while the concentration ranges, size and origin (e.g. production technology) of nanoparticles are still unknown (Shrivastava et al., 2019; Kumahor et al., 2015).

Up until now, environmental studies focused almost exclusively on the effect of engineered nanoparticles on biota (Bundschuh et al., 2018; Grün et al., 2018; Seitz et al., 2015). In general, some engineered nanoparticles were found to be toxic for yeasts, bacteria, fungi, marine diatom, fish, the root system of higher plants (Rajput et al., 2017), or to affect the composition and stability of freshwater biofilms (Grün et al., 2018). In soils, an adverse effect was observed, among others, on the abundance, diversity and structure of bacterial communities and enzymatic activities (Buzea et al., 2007) as well as on biological nitrogen fixation (Xu et al., 2015). However, the effect on properties and functions of affected environmental compartments is still overlooked. This is understandable because environmental compartments are complex systems, and it is difficult to distinguish between natural colloids and engineered nanoparticles (Bundschuh et al., 2018; Philippe et al., 2018; Philippe and Schaumann, 2014).

One of the most affected environmental compartments is soil organic matter (SOM), which is responsible for most of the soil's ecological functions (Wiesmeier et al., 2019), which are determined by the nanoscopic scale properties of SOM (Navrotsky, 2003a). From the physicochemical viewpoint, SOM is a heterogeneous multiphase and porous system with uneven distribution of functional groups and hydrophobic hotpots, which is developed from biomass under biotic and abiotic conditions. SOM pores' configuration influences aeration, reactivity, water holding capacity and the fate of adsorbed molecules (de Jonge and Mittelmeijer-Hazeleger, 1996; Pignatello, 1998). The organic soil components that cannot be bridged directly, may interact with each other via water molecule bridges (WaMB) consisting of water clusters, where several water molecules are held together by the H-bonds between them, and with the polar groups of SOM (Jäger et al., 2016; Schaumann, 2006; Schaumann and LeBoeuf, 2005). The formation of bridges decreases the mobility of SOM moieties, thereby increasing the rigidity of SOM's physical structure (Kučerík et al., 2014). WaMB appeared to be very important for the structural physicochemical aging of SOM (Jaeger et al., 2015; Kučerík et al., 2014). Recently, it was found that the WaMB stability correlates positively with the time constant of phenol desorption, which implies that WaMB governs the fate of adsorbed volatile organic compounds (Ondruch, 2018; Ondruch et al., 2019).

Under arid conditions, three types of water occur in SOM: a monolayer of water adsorbed on primary sorption sites, WaMB, and the so-called phase water resembling bulk water. WaMB is formed as a secondary layer on primary sorption sites and governs the amount of phase water in SOM under arid conditions (Kučerík et al., 2018). A gradual increase in phase water content leads to SOM swelling and WaMB interruption (Kunhi Mouvenchery et al., 2013). Molecular modeling revealed that WaMB consists of tens of molecules and is formed primarily between groups that are less than 2 nm apart (Aquino et al., 2011a, 2011b; Aquino et al., 2009). Therefore, properties of WaMB and consequently, phase water, are indicators for the correct functioning of SOM and sensitive indicators of soil contamination (Ondruch et al., 2017b).

An important feature of nanoparticles is that their surface properties can deviate markedly from those shown by both their macroscopic (bulk) and atomic (cations) counterparts, thereby significantly influencing their chemical and physicochemical characteristics. This is particularly true when their particle size decreases below ~ 10 nm (Wiesner et al., 2011; Zhang et al., 2003). Furthermore, the natural colloids are under environmental conditions (mostly negatively charged or containing groups prone to easy dissociation (Avena et al., 1999)), which leads to reversible interactions with SOM moieties (Navrotsky, 2003a; Philippe and Schaumann, 2014).

A pronounced function of SOM is water management, which is related to its microporosity (Borisover, 2013; Borisover and Graber, 2004; de Jonge and Mittelmeijer-Hazeleger, 1996). To the best of our knowledge, the literature overview shows no relevant information on the effect of small-sized nanoparticles on SOM and its function to retain and control water.

In this pilot study, results about the influence of platinum (Pt) nanoparticles on water properties in SOM are initially shown. The concentration of Pt nanoparticles in soils is gradually increasing due to releases from car engines (Komendova and Jezek, 2019). Pt is released in the form of particles having sizes ranging predominantly between 0.3 μm and 25 nm (Prichard and Fisher, 2012). These are further disintegrated into smaller pieces and may dissolve in organic acids (Bowles and Gize, 2005). For this reason, 3 nm sized particles that are also close to the pore diameter in which WaMB are formed, were tested for their effect on water in SOM. In general, the smaller the nanoparticles are, the more they expose atoms in less stable planes, giving rise to a steep increase in surface free energy. Accordingly, the 3 nm Pt nanoparticles have a high surface energy (Vitos et al., 1998), which causes a strong affinity to water (Navrotsky, 2003b). The strong hydration is connected with the local strengthening of H-bonds, which is compensated for by the weakening of H-bonds in other regions (Chaplin, 2007). This is a result of compensation between the H-bond's attractive energy (enthalpy contribution) and the energy required for creating the orderliness apparent in water cluster formation (entropy contribution) (Chaplin, 2007).

Accordingly, we hypothesize that (i) Pt nanoparticles act as kosmotropic agents (structure-forming) on short distances (i.e. small water volumes of WaMB) and as chaotropic agents (i.e. water structure destructuring) on long distances (i.e. large water volumes of phase water). As aforementioned, nanoparticles in SOM rarely occur as discrete entities (Theng and Yuan, 2008), but they interact with SOM moieties, which decrease their surface energy (Zhang et al., 2003). This implies the second hypothesis (ii) that the interaction with SOM decreases the influence of Pt nanoparticles on water properties. The properties of water play an important role in soil processes and soil functions (effect on climate, biota, etc.) (Makarieva et al., 2013). For this reason, it is necessary to understand the consequences of this type of contamination.

The soil is composed of particles with different sizes, reactivity and composition that form a complex hierarchical porous structure.

Therefore, the analysis of nanoparticles on soil properties requires either the use of a multitude of methods (Shrivastava et al., 2019) or a focus on particular soil compartments. In this study, to avoid the effect of minerals on nanoparticles, an organic soil (a sapric histosol) that contains almost exclusively organic matter and low amount of minerals was used as a model soil. The properties of water in this soil were recently investigated in detail (Kučerík et al., 2018). Thus, it can be used as a model for the evaluation of water and nanoparticles in SOM. The effect of Pt nanoparticles in a wide range of concentrations was analyzed to determine the threshold concentration at which nanoparticles begin to influence the water content, evaporation enthalpy, ice melting enthalpy and stability of water molecule bridges. These properties were chosen to represent the most important parameters describing water properties in soil under arid and semi-arid conditions. Differential Scanning Calorimetry (DSC) was employed to analyze the effects of Pt nanoparticles on properties of water in the soil. DSC has repeatedly been shown to provide reliable data with clear physical meaning and is already established in this type of research (Kunhi Mouvenchery et al., 2013; Schaumann, 2005; Schaumann and LeBoeuf, 2005; Vojta et al., 2016).

2. Material and methods

2.1. Soil

A clay-free organic sapric histosol, collected from Totes Moor (located ~30 km northwest of Hannover, Germany) and consisting of peat bog and fen areas, was used. This soil has been comprehensively characterized in previous works (Jäger et al., 2011; Kunhi Mouvenchery et al., 2013; Ondruch et al., 2017b; Schaumann et al., 2013). It contains 52% and around 6.8% of organic carbon and ash, respectively. Its cation exchange capacity is 123 mmol kg^{-1} and pH ($CaCl_2$ 0.01 M) is 2.7 (Schaumann et al., 2013). A recent study (Ondruch et al., 2017b) showed that 63% of functional groups in sapric histosol are O-Alkyl, N-Alkyl; O-Aryl, N-Aryl and carbonyl and carboxylic moieties, 15% of moieties are aryl-H and aryl-C carbons, and olefinic-C, and 22% are alkyl-C moieties, which is comparable to other histosols and SOM in forest soils.

The sapric histosol was air-dried, ground in an agate mortar and sieved with a sieve with a mesh size of 100 μm. Then, 300 mg of this soil was weighed into glass vials, and various concentrations of the aqueous dispersion of platinum nanoparticles each with a total volume of 1 mL were added, gently stirred and dried according to the procedure specified further below. The following amounts of Pt (in μg) per 300 g of sample were used: 0, 0.1, 1, 10, 100, 1000. This means that resulting concentrations were concentrations of 0, $3.3\ 10^{-4}$, $3.3\ 10^{-3}$· $3.3\ 10^{-2}$ $3.3\ 10^{-1}$ $\mu g_{Pt}\ g_{soil}^{-1}$. However, for easier comparison, concentrations are reported as 0, 0.1, 1, 10, 100, 1000 in μg_{Pt} 300 g_{soil}^{-1} further in the text. Each mixture was prepared in triplicate and consequently transferred into a container with controlled relative humidity (RH), where it was kept for five weeks to equilibrate the relative humidity. Three different RHs were maintained by using saturated salt solutions: 95% using a saturated solution of KNO_3, 76% using NaCl and 43% using K_2CO_3.

2.2. Adsorption isotherm

Sorption capacity of Pt on soil was tested to determine the adsorption isotherm (see Supporting Information, Fig. S1). Briefly, 300 mg of dried and sieved soil was mixed with 1 mL of a nanoparticle suspension of platinum in water, in a concentration range of 0.1–1000 mg L^{-1}. The mixture was left for one week. The suspension was filtered, and the content of unbound platinum (including the content adsorbed on the filter) was analyzed on a ContrAA 800 atomic absorption spectrometer (Jena, Germany). The measurement conditions were as follows: Pt 265.9450 nm, dosing 20 μL, and furnace program: drying 80 °C, 90 °C, 110 °C, pyrolysis 350 °C, 1300 °C, atomize 2300 °C, and clean 2450 °C. Calibration was performed on the nanoparticles of Pt in water, and the Limit of Detection (LOD) was 1.277 μg l^{-1}.

2.3. DSC analysis

DSC Q2500 equipped with a cooling system RCS90 (TA Instruments, New Castle, Delaware) was used for all analyses. The sample holders were aluminum Tzero pans, and the reference used was always a pan of the same type. The system was calibrated for temperature and enthalpy, using indium standard, and verified by melting temperatures and enthalpies of Zn, Sn and ice. In all experiments, nitrogen (purity 5.0) was used as a purge and protective gas at a flow rate of 50 mL min^{-1}. Three replicate measurements were conducted for each sample. The obtained records were evaluated using TRIOS software from TA Instruments.

The stability of WaMB in soils is proportional to structural stiffness. Traditionally, it is determined as a temperature of its disruption. The disruption can be determined as the temperature of a step increase in heat capacity, which corresponds to the change in measured heat flow. The onset temperatures of WaMB disruption (T_{onset}) were determined. As the distances between functional groups in SOM differ, there is a distribution of WaMB in SOM, and the T_{onset} refers to the WaMB of the lowest stability (Kučerík et al., 2018). WaMB was determined by the measurement of about 5 mg of soils in hermetically sealed containers. The following temperature regime was applied: cooling to −50 °C at 10 °C min^{-1}, followed by heating to 110 °C at 10 °C min^{-1}; then the sample was cooled again to −50 °C at the cooling rate 10 °C min^{-1}, and heated again to 110 °C at 10 °C min^{-1}. An example of onset determination is reported in Fig. S1b (SI).

Water desorption enthalpy is proportional to the strength of water binding in SOM (Kučerík et al., 2018). The soil samples were weighed and hermetically sealed in aluminum pans. Prior to the measurements being taken, the lids were perforated with a sharp pin, the pan was immediately loaded into the DSC, and the following protocol was applied: cooling to −50 °C at 10 °C min^{-1} and then heating to 200 °C at 5 °C min^{-1}. A hermetically sealed empty pan was used as a reference. The sample pan was weighed before and after the DSC analysis so that the mass difference reflected the moisture content.

In the soil where the formation of phase water was observed, its freezing enthalpy was also determined, which reflects the character of water structure in pores (Kučerík et al., 2012). Briefly, if the run for WaMB stability determination also contained an endotherm occurring at around 0 °C, the peak was integrated, and enthalpy of the process was determined.

The evaporation and melting enthalpy of a droplet of pure water and nanoparticles suspension 1000 mg L^{-1} (sample weight ~3 mg) were measured in the same way. All the samples were measured under similar atmospheric pressure.

Because of a shift in the baseline caused by a change in the heat capacity and sample mass during water elimination, the endotherm obtained during the measurement was integrated with a sigmoidal tangential baseline included in the TRIOS (TA Instruments) software. The determined enthalpy in Joules (J) was divided by the mass of water obtained as a difference between the sample mass weighed before and after the measurement. An exemplary record is reported in Fig. S1c (SI). This method was previously developed and tested for the characterization of water in polysaccharides and humic acids (Cihlář et al., 2016; Prusova et al., 2010).

The content of the aliphatic crystallites was estimated from an endothermal peak corresponding to their melting enthalpy observed in the second run (Kučerík et al., 2014).

2.4. Molecular modeling

The modeling of the interaction between Pt nanoparticles and WaMB was performed to explain the observed influence of nanoparticles on the enthalpy of water evaporation. The modeled system comprised of a spherical particle with a variable diameter ranging from 0.4 to 4 nm in the center of a cubic box with a length of 5 nm. The spherical particle was composed of Pt atoms ordered to the Face Centered Cubic lattice (FCC, lattice constant 0.39229 nm). There was also a cluster of several water molecules mimicking WaMB in the model. The cluster was bound on a pair of COOH groups representing SOM. Each COOH group was attached to a short hydrocarbon chain (-CH_2-CH_2-, approximate length of chain 0.3 nm). The radius of the motion of the COOH group around the particle was limited by the length of the short chain. Lastly, in the modeling were 1500 molecules of water distributed randomly in the box around the particle. They represented phase water.

The coordinates of Pt atoms and one end of the hydrocarbon chain were fixed. The interaction of water molecule with Pt particle is considered as non-bonding Lennard-Jones potential with potential energy 9 kJ mol^{-1} (Michaelides, 2006). The pair interaction, water-water and water-COOH group, were of the electrostatic type. The partial charges on water molecules were taken from the SPC-E model: O (-0.8476 of elementary charge), and H ($+0.4238$e). The charges on the COOH were distributed C ($+0.61$e), carbonyl O (-0.64e), hydroxyl O (-0.17e), and H ($+0.20$e).

The modeling was carried out for two temperatures 300 and 600 K, which was the limit case of the water in the gas state. The water molecules were randomly dispersed in the simulation box. At 300 K water was in the liquid state and all the molecules were condensed on the surface of the particle. The evaporation energy was calculated as a difference of the potential energies between the gas and liquid phases:

$$\Delta E = E_{\mathrm{p,gas}} - E_{\mathrm{p,liquid}} \tag{1}$$

The result is the difference of potential energy during evaporation of water, while the ΔE of Pt atoms is constant, and the difference for WaMB is negligible.

Next, evaporation energy ΔE_0 of the system particle/water with and without WaMB was calculated. Accordingly, the resulting contribution of WaMB (ΔE_{wb}) to the evaporation was calculated as follows:

$$\Delta E_{\mathrm{wb}} = \Delta E - \Delta E_0 \tag{2}$$

3. Results and discussion

3.1. The effect of 3 nm platinum nanoparticles on the properties of pure water

First, the evaporation enthalpy of a droplet of pure water (~3 mg) containing 1000 mg L^{-1} Pt nanoparticles was measured to analyze the effect of the nanoparticles on pure water. The resulting values for pure water and nanoparticles suspension were 2.2 ± 0.1 and 1.9 ± 0.2 kJ g^{-1}, respectively. Afterwards, the melting enthalpy of ice from pure water and Pt nanoparticles were measured, resulting in 333 ± 3 and 106 ± 7 J g^{-1}, respectively. These results indicate that Pt nanoparticles can influence water structure, and it is important to observe the effect in the presence of SOM.

3.2. The effect of 3 nm platinum nanoparticles on the amount and type of water in soil organic matter

An important SOM function under arid conditions is its water holding capacity, which is influenced by the abundance, type and distribution of functional groups, and porosity (Kučerík et al., 2018). Fig. 1 reports the amount of water adsorbed at different RH without (the solid line represents averaged value, and the dashed lines represent the standard deviations) and with the presence of nanoparticles. It was found that at 43 and 79% RH, 3 nm Pt nanoparticles did not affect the amount of the water content. However, a significant decrease in water content was observed at 96% RH at high nanoparticles concentrations (between 100 and 1000 μg Pt 300 $\mathrm{mg}_{\mathrm{soil}}^{-1}$). This corroborates with the adsorption isotherm reported in Fig. S2 (SI) that shows that the ratio between adsorbed amount of Pt nanoparticles and stock solutions is constant up to the concentration level of 10 μg Pt 300 $\mathrm{mg}_{\mathrm{soil}}^{-1}$, while above this concentration, the adsorption capacity decreases, i.e. the soil contains larger amount of free particles.

Water is present in three overlapping and interrelated states in SOM exposed to different RH (Kučerík et al., 2018). In dried SOM exposed to low relative humidity (i.e. below and around 43%), water molecules are

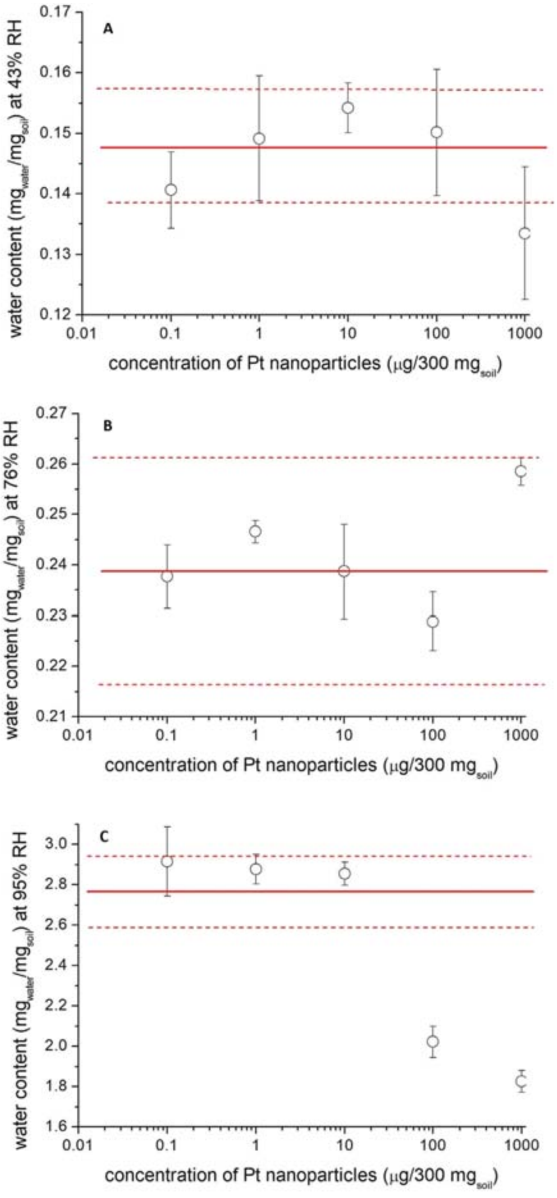

Fig. 1. Effect of Pt nanoparticles on water content in sapric histosol at A) 46%, B) 76% and C) 95% RH.

strongly bound to primary sorption sites (Langmuir-like adsorption). H-bonds and electrostatic coulombic interactions occur preferentially between water and polar functional groups. The relative humidity increment allows a second form of water that is WaMB. As aforementioned, WaMB is made of water clusters bridging the functional groups that are not close enough to interact directly. In WaMB, water-water interactions are predominant. The conformational organization of the water molecules in the bridges depends on the nature of the hydrophilic systems with which they interact (Conte, 2019). An increase in relative humidity causes a further increase in the number of water molecules involved in WaMB, leading to its destabilization due to the progressive formation of phase water and SOM swelling. In this study, a larger content of phase water was observed in soil dried at 95% RH for five weeks. The phase water could be identified in the form of ice, which exhibits an endothermal peak around 0 °C while melting (Kučerík et al., 2012) (Fig. S1a). The evaporation enthalpy of water from a blank sample compared to recent results (Kučerík et al., 2018) suggests that SOM also exposed to 76% RH contains a small amount of phase water.

3.3. The effect of 3 nm platinum nanoparticles on the structural rigidity of SOM (stability of WaMB)

The structural rigidity of SOM governs the fate of pollutants (Pignatello, 1998) and SOM structural physicochemical aging (Jaeger et al., 2015; Kučerík et al., 2014), and correlates positively with the thermal stability of WaMB (Schaumann, 2006).

Exemplary measurements of WaMB stability in samples with 100 μg Pt 300 $\mathrm{mg}_{\mathrm{soil}}^{-1}$ at RH 43, 76 and 95% are reported in Fig. S1a (SI). The records show that WaMB transition, i.e. step-like transition starting at around 50 °C, can be observed in soil exposed to a relative humidity of 43 and 76%. Soil exposed to 95% RH showed an endothermal peak at around 0 °C and an unmeasurable WaMB transition. Fig. S1b (SI) shows the exemplary determination of WaMB $\mathrm{T}_{\mathrm{onset}}$ corresponding to WaMB stability. Fig. 2 reports an increase in WaMB stability with increasing concentration of 3 nm Pt nanoparticles. This trend was more pronounced in soil exposed to 43% RH.

An increase in WaMB stability (reflected by an increase in the $\mathrm{T}_{\mathrm{onset}}$, Fig. 2) with increasing concentration reflects an increase in SOM structural rigidity upon contamination by Pt nanoparticles, resembling the reinforcement of polymeric nanocomposites (Jancar et al., 2013). The nanoparticles below 10 nm are strongly hydrated (Navrotsky, 2003b), which facilitates their penetration between functional groups and their incorporation into the WaMB. As a result, WaMB stability ($\mathrm{T}_{\mathrm{onset}}$) significantly increases. In other words, platinum works as a kosmotropic agent for water in a WaMB hotspot, i.e. in a small volume. We hypothesize the formation of a rigid ice-like shell around the nanoparticle. The structure is not flexible enough to sustain H-bonds among water molecules in the first hydration layer, but the strong $\mathrm{Pt\text{-}OH_2}$ interactions induce high polarization of the oxygen atoms in the water molecules coordinated to the metal. As a consequence, stronger hydrogen bonds with adjacent water molecules in the second hydration shell are formed (Conte and Nestle, 2015).

3.4. The effect of 3 nm platinum nanoparticles on water evaporation enthalpy

The strength of water binding is a decisive factor for water management in SOM under both arid and semi-arid conditions (Cihlar et al., 2014). Here, the effect of Pt nanoparticles in SOM was also observed on the strength of water binding represented by evaporation enthalpy (Fig. 3; an exemplary record is reported in Fig. S1c (SI)). In general, the obtained evaporation enthalpy is a sum of interaction energies, which prevent water molecules from evaporation and consists of a contribution from all the interactions between SOM, water and nanoparticles. In particular, no change in the whole concentration range was observed in the soil exposed to 43% RH (Fig. 3). Conversely, at 76% RH, evaporation enthalpy decreased in comparison to a blank at 10 μg μg Pt 300 $\mathrm{mg}_{\mathrm{soil}}^{-1}$ and above this concentration. In soil exposed to 95% RH, enthalpy decreased at 0.1 μg Pt 300 $\mathrm{mg}_{\mathrm{soil}}^{-1}$ and above this concentration.

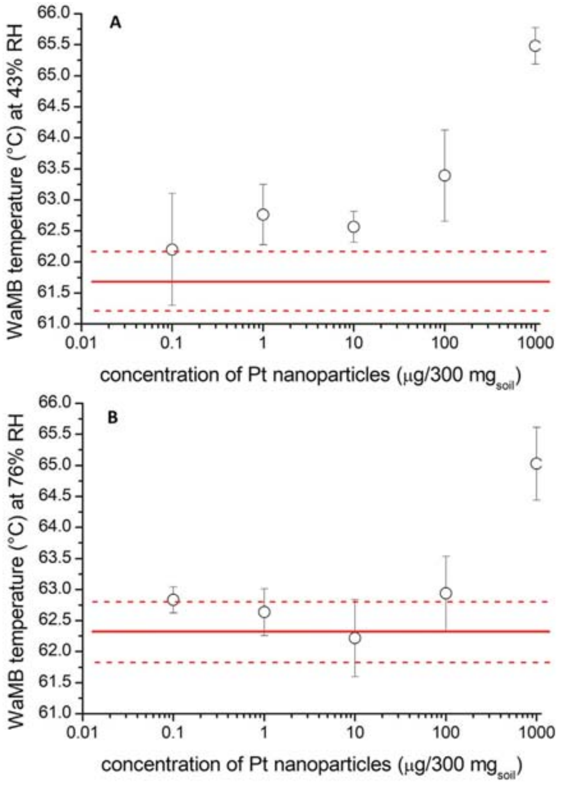

Fig. 2. Effect on the stability of WaMB in soils dried at A) 43% and B) 76% RH.

Results in Fig. 2 show that WaMB stability increased more at lower RHs, which is in contrast to the evaporation enthalpy, which decreased at higher RHs (Fig. 3). The decrease in evaporation enthalpy was observed in the whole investigated concentration range in SOM dried at 95% RH. In soil dried at 76% RH, a statistically significant decrease was observed at 10 μg of Pt nanoparticles per 300 mg of soil and above this concentration. These observations imply that phase water in SOM is influenced similarly as in pure water. Therefore, the hypothesis that the interaction with soil would compensate for the effect of nanoparticles on water properties was not confirmed at higher RH. In addition, the results show that Pt nanoparticles act as chaotropes in phase water, i.e. in larger volumes. The decrease in evaporation enthalpy of water containing nanoparticles corroborates with the results of Volkov et al. (2015a, 2015b) and Narvaez et al. (2014), who observed an intensification of heat-up and an increase in the rate of the evaporation processes of a water droplet containing suspended titanium dioxide and alumina nanopowders, respectively. The explanation of this phenomenon includes considerations about an increase in thermal conductivity caused by particles, an increase of radiant heat flux to the surface of the "heterogeneous" water droplet, the movement of particles from a heated surface to deeper (colder) regions in a droplet, and the consequent heating of the environment of particle surface (Volkov et al., 2015b). Besides, the rate of evaporation was found to depend strongly on the heating mechanisms (Kuznetsov et al., 2018). However, neither an increase in thermal conductivity nor radiant heat flux to the surface of

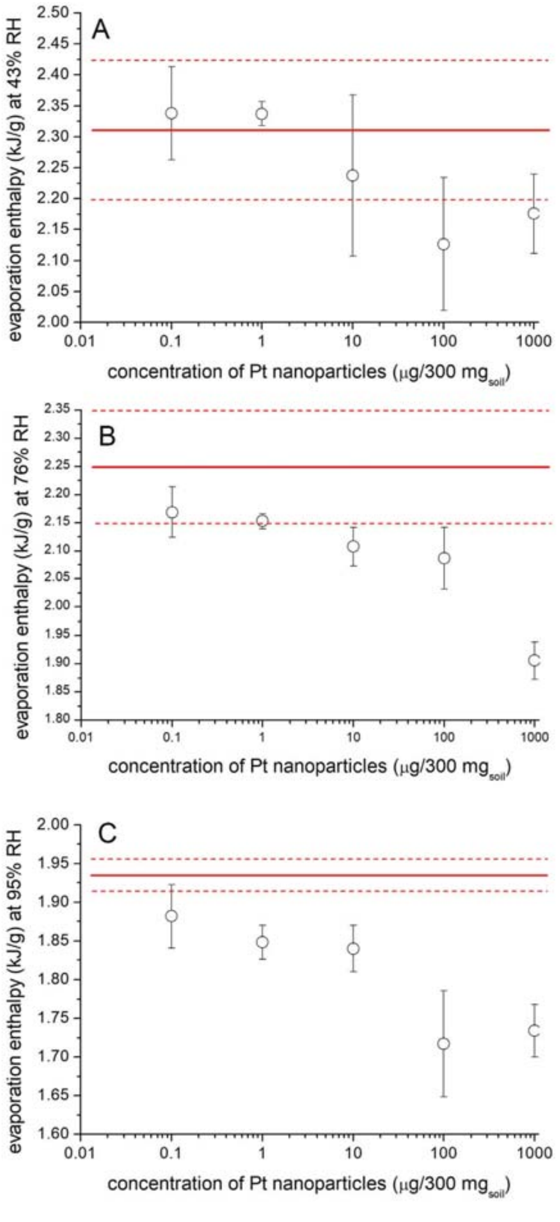

Fig. 3. Effect of Pt nanoparticles on evaporation enthalpy in soils contaminated by 3 nm Pt nanoparticles exposed to A) 43%, B) 76% and C) 95% relative humidity.

the nanoparticle would have explained the observed decrease in evaporation enthalpy and increase in WaMB stability. On the contrary, the overheating of a particle would lead to a decrease in WaMB thermal stability observed in this work. For this reason, a more suitable explanation of the effect of Pt nanoparticles on water 3D structure was considered.

3.5. The effect of 3 nm platinum nanoparticles on ice structure

Ice is a highly ordered but loose structure of water molecules stabilized by H-bond interactions, which result from the structure of water in the liquid state and which can be perturbed by the presence of solutes (Cataliotti et al., 2009) or by confinement in porous structures (Majda et al., 2017). Under standard conditions, the hexagonal symmetry of ice is formed from pure water with melting enthalpy of 333 J g^{-1}. Therefore, a change in this value reflects a change in the liquid water structure.

The endotherm in Fig. S1a (SI) shows that soil exposed to 95% RH contains phase water, which can freeze upon cooling. The melting enthalpy is indicative for ice structure, and results showed constant values up to 10 μg Pt 300 mg$_{\text{soil}}^{-1}$ and decreased values at and above 100 μg Pt 300 mg$_{\text{soil}}^{-1}$ (Fig. 4).

The enthalpy of ice melting reported in Fig. 4 supports the conclusion about the chaotropic effect of Pt nanoparticles in phase water. Standard ice melting enthalpy, i.e. the ice hexagonal crystalline structures, is around 333 J g^{-1}. The decrease of melting enthalpy in comparison to standard ice melting (333 J g^{-1}) in Fig. 4 is an indication of the disruption of the ice structure, though it is not as intense as in the pure water, which gave 106 ± 7 J g^{-1}. The concentration at 100 μg Pt 300 mg$_{\text{soil}}^{-1}$ corroborates with the results of adsorption isotherm, which showed that at and above this concentration, free Pt nanoparticles may occur in SOM.

The discrepancy in the concentrations at which nanoparticles influence the water properties for evaporation (0.1 μg Pt 300 mg$_{\text{soil}}^{-1}$) and melting (100 μg Pt 300 mg$_{\text{soil}}^{-1}$) can be attributed to the fact that during evaporation the Pt concentration steadily increases, and the value therefore reflects the influence of both low and high concentrations.

3.6. The effect of 3 nm platinum nanoparticles on aliphatic crystallites

Aliphatic crystallites represent a still not well-understood part of SOM. The aliphatic carbon content increases with increasing SOM decomposition (Deshmukh et al., 2005) and in a crystalline form is expected to be resistant to environmental attack (Hu et al., 2000). However, some studies reported that the content of aliphatic crystallites can easily be changed (both increased and decreased) by various polar and apolar contaminants (Ondruch et al., 2017a). Also, in this study, the content of aliphatic crystallites was changed upon interaction with 3 nm Pt nanoparticles. Fig. S3 (SI) shows that the enthalpy of the endothermal peak detected in the second run changed. It was found that the effect is more pronounced at 76% RH, where it can be observed at 10 μg of Pt per 300 mg$_{\text{soil}}^{-1}$. The crystallites consist of biopolymer residues from higher plants and lipids presumably of microbiological origin (Ondruch et al., 2017a), and the increase in their melting enthalpy in Fig. S3 (SI) can be interpreted that Pt nanoparticles induce their crystallization. Comparing the results to recent work in which both polar and apolar contaminants were used (Ondruch et al., 2017a), the effect

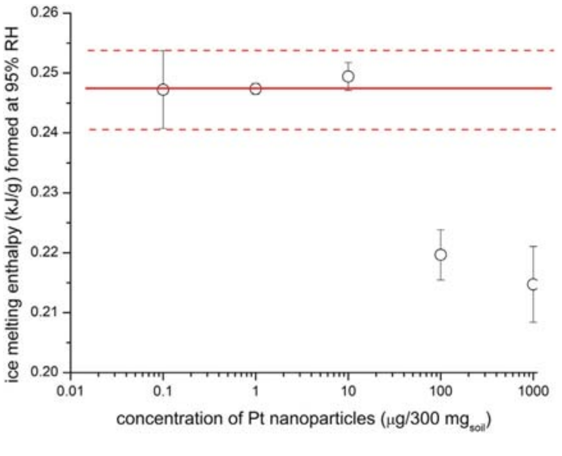

Fig. 4. Effect of concentration of 3 nm Pt nanoparticles on the ice melting enthalpy in soil exposed to 95% RH.

induced by Pt nanoparticles is much more significant. Currently, there is no explanation for these observations, but it is hypothesized that it may be a result of the effect of free nanoparticles (Fig. S2, SI).

3.7. Molecular modeling

Water adsorption was investigated by molecular modeling (Fig. 5). Each model is a combination of three types of objects (Pt nanoparticle, WaMB and water molecules), where each component gives its own contribution to the potential energy to evaporation, ΔE_{wb}. Fig. 5a shows the influence of particle size, which can either increase (positive effect) or decrease (negative effect) the evaporation enthalpy. The switch between positive and negative effect was observed above 1 nm. Increasing the particle size to 4 nm slowly decreases the negative effect. Fig. 5b shows an increase in ΔE_{wb} with increasing concentration of WaMB present on the surface of a Pt nanoparticle. Here the switch from negative to positive values occurred at around 0.4 WaMB per nm^2. The results support the conclusions based on the DSC results about the orientation of water on the Pt nanoparticle, i.e. kosmotropic effect. In fact, ΔE_{wb} values indicate that at a certain size, the WaMB on Pt nanoparticles suppresses the water evaporation, which is probably caused by the WaMB structure. Smaller-sized nanoparticles are encapsulated in a cluster (WaMB) of similar size, and the system is thermodynamically stable. Increasing the nanoparticle size opens the cluster, and the WaMB is disrupted (Fig. 5a). Increasing the number of WaMB on the nanoparticle surface (Fig. 5b) increases the stability of WaMB and the energy of the system increases. In summary, the ΔE_{wb} is influenced by both nanoparticle size and the number of WaMB on the nanoparticle surface. For 3 nm nanoparticles, the result is negative, and the functional groups in the SOM act against the decrease in evaporation enthalpy via WaMB. However, it is overcompensated by the size of Pt nanoparticles (Fig. 5b). The results also imply that certain conditions, such as decreasing the nanoparticles' size (approximately below 1.5 nm), may cause an opposite effect, i.e. they can increase the evaporation enthalpy, thereby preventing fast desiccation.

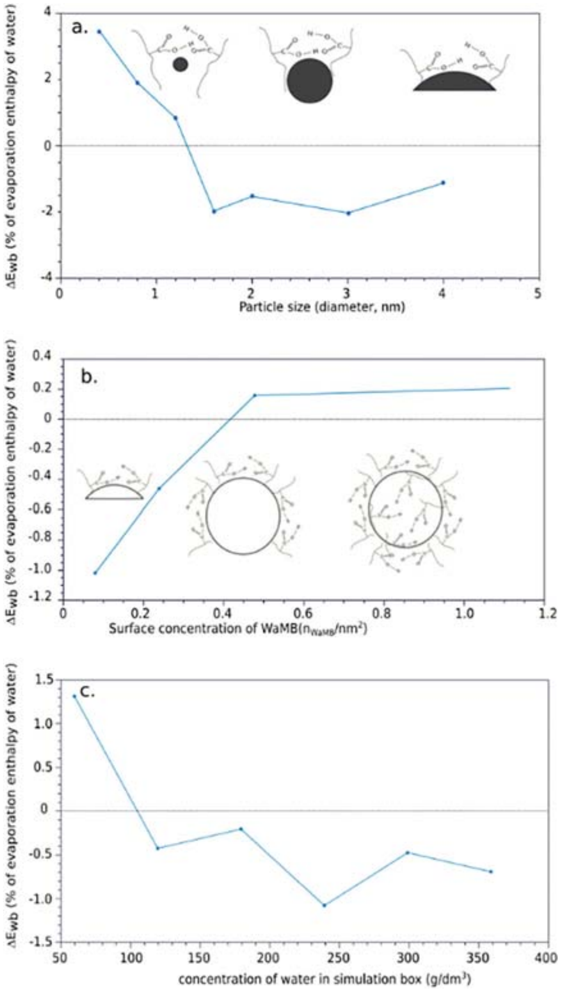

Fig. 5. Molecular modeling results: influence of WaMB to the evaporation enthalpy; a) effect of particle size; b) effect of surface concentration of WaMB; c) effect of water concentration in simulation box.

Fig. 5c reports a decrease in ΔE_{wb} dependence on the amount of phase water, while the switch from positive to negative values was observed for phase water consisting of around 100 g dm^{-3} continuing irregularly to 370 g dm^{-3}, which was the maximum amount of water molecules used for the modeling. These observations support the conclusion that in larger values, the Pt nanoparticles act as chaotropes.

3.8. Possible environmental relevance

The aim of this study was to show that the risk of contamination of the environment by nanoparticles may also be observed from the point of view of their influence on the physicochemical parameters of SOM and water properties. Nevertheless, to proceed further proceed with this subject, it is important to test other variables. Among the most important are (i) to test the effect of nanoparticles on mineral soils, where the inorganic components such as SiO_2 can cause other effects (Engemann et al., 2004), (ii) to test other types of nanoparticles, (iii) to test different types of SOM, because the sapric histosol investigated in this work was very acidic compared to other soil types (although it gives similar results as other peat and forest soils) (Ondruch et al., 2019) and (iv) to test the effects in soils contaminated by nanoparticles for a longer time, because in this work, the samples were freshly prepared, and the microbiological processes were largely suppressed.

The results obtained in this study led to several conclusions. The natural levels of Pt metals in the environment are generally less than 1–3 ng g^{-1} (Jackson et al., 2007). The anthropogenic contamination increases platinum concentration (Komendova and Jezek, 2019) while the particle size depends on the density of car traffic and distance from route, respectively (Prichard and Fisher, 2012). In areas with high transport density, there were determined Pt concentrations at around 10 ng g^{-1}. Special situations occur in tunnels or places without climatic influences (underpasses), where platinum accumulates and its concentration reaches values higher than 100 ng g^{-1} (Komendova and Jezek, 2019). In road dust, the concentration reached 2000 ng g^{-1} (Prichard and Fisher, 2012). In this work, we analyzed the influence of Pt in a model SOM. However, the content of SOM is in mineral soils about one or two orders lower. This means that the concentration at around 1 μg g^{-1} is approaching environmentally relevant content. Additionally, the Pt particles emitted to the environment are gradually eroded, and the formed nanoparticles can locally reach a high concentration in hotspots in environments with low water concentrations. This nanoparticles concentration can further increase due to water evaporation.

As understood from previous works (Kuznetsov et al., 2018; Volkov et al., 2015b), the influence of nanoparticles on the rate of water evaporation is a frequent phenomenon. The pilot study carried on Pt nanoparticles showed a decrease in evaporation enthalpy. Thus, it is hypothesized that other more frequently used engineered and widespread nanoparticles, such as zero metal and metal oxide and carbonaceous nanoparticles, may also have similar effects on water properties in soil.

4. Conclusion

Currently, the amount of airborne nanoparticles in rural and urban areas spans from 10^6 to 10^8 nanoparticles per liter of air, depending on the air conditions (Buseck and Adachi, 2008). Therefore, soils are constantly exposed to contamination of nanoparticles, which is more intense in the vicinity of waste disposal and other sources of contamination (Bakshi et al., 2015; Šesták et al., 2010). In light of the above discussion, nanoparticles, unlike chemicals, may affect the local physicochemical processes in soils, accelerate the soil desiccation, thereby contributing to enhanced evapotranspiration, and potentially influence other soil processes. The model study presented here focused on Pt nanoparticles originating mostly from car engines, which represent only a minor part of nanoparticles released to the environment. However, as understood from previous works, similar effects were also observed for other types of nanoparticles. Therefore, further research is needed to investigate the relationship between the types, sizes and concentrations of nanoparticles and water physicochemical constants to be able to predict their effect on various environmental compartments.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supporting information contains Fig. S1 a) comparison of DSC records of 100 μg per 300 mg of soil at different RH, b) an example of determination of WaMB stability, c) an example of determination of strength of water binding (evaporation), d) comparison of ice melting for blank, 100 and 1000 μg per 300 mg of soil. Fig. S2 shows the adsorption isotherm of platinum nanoparticles on soil organic matter. Fig. S3 shows the effect of the 3 nm Pt nanoparticles on melting enthalpy of aliphatic crystallites. Supplementary data to this article can be found online at doi:https://doi.org/10.1016/j.scitotenv.2019.133822.

References

Aquino, A.J.A., Tunega, D., Schaumann, G.E., Haberhauer, G., Gerzabek, M.H., Lischka, H., 2009. Stabilizing capacity of water bridges in nanopore segments of humic substances: a theoretical investigation. J. Phys. Chem. C 113, 16468–16475. https://doi.org/10.1021/jp9054796.

Aquino, A.J.A., Tunega, D., Pašalić, H., Schaumann, G.E., Haberhauer, G., Gerzabek, M.H., Lischka, H., 2011a. Study of solvent effect on the stability of water bridge-linked carboxyl groups in humic acid models. Geoderma 169, 20–26. https://doi.org/10.1016/j.geoderma.2010.12.006.

Aquino, A.J.A., Tunega, D., Pašalić, H., Schaumann, G.E., Haberhauer, G., Gerzabek, M.H., Lischka, H., 2011b. Molecular dynamics simulations of water molecule-bridges in polar domains of humic acids. Environ. Sci. Technol. 45, 8411–8419. https://doi.org/10.1021/es201831g.

Avena, M.J., Koopal, L.K., van Riemsdijk, W.H., 1999. Proton binding to humic acids: electrostatic and intrinsic interactions. J. Colloid Interface Sci. 217, 37–48. https://doi.org/10.1006/jcis.1999.6317.

Bakshi, S., He, Z.L., Harris, W.G., 2015. Natural nanoparticles: implications for environment and human health. Crit. Rev. Environ. Sci. Technol. 45, 861–904. https://doi.org/10.1080/10643389.2014.921975.

Borisover, M., 2013. The effect of organic sorbates on water associated with environmentally important sorbents: estimating and the LFER analysis. Adsorption, 241–250 https://doi.org/10.1007/s10450-012-9446-7.

Borisover, M., Graber, E.R., 2004. Hydration of natural organic matter: effect on sorption of organic compounds by Humin and humic acid fractions vs original peat material. Environ. Sci. Technol. 38, 4120–4129. https://doi.org/10.1021/es035357s.

Bowles, J.F.W., Gize, A.P., 2005. A preliminary study of the release of platinum and palladium from metallic particles in the surface environment by organic acids: relevance to weathering of particles from vehicle exhaust catalysts. Mineral. Mag. 69, 687–693. https://doi.org/10.1180/0026461056950280.

Bundschuh, M., Filser, J., Lüderwald, S., McKee, M.S., Metreveli, G., Schaumann, G.E., Schulz, R., Wagner, S., 2018. Nanoparticles in the environment: where do we come from, where do we go to? Environ. Sci. Eur. https://doi.org/10.1186/s12302-018-0132-6.

Buseck, P.R., Adachi, K., 2008. Nanoparticles in the atmosphere. Elements 4, 389–394. https://doi.org/10.2113/gselements.4.6.389.

Buzea, C., Pacheco, I.I., Robbie, K., 2007. Nanomaterials and nanoparticles: sources and toxicity. Biointerphases 2, MR17–MR71.

Cataliotti, R.S., Aliotta, F., Ponterio, R., 2009. Silver nanoparticles behave as hydrophobic solutes towards the liquid water structure in the interaction shell. A Raman study in the O-H stretching region. Phys. Chem. Chem. Phys. 11, 11258–11263. https://doi.org/10.1039/b915317a.

Chaplin, M.F., 2007. Water's Hydrogen Bond Strength. Soft Condens. Matter cond-mat.s 1–20.

Cihlar, Z., Vojtova, L., Conte, P., Nasir, S., Kucerik, J., 2014. Hydration and water holding properties of cross-linked lignite humic acids. Geoderma 230–231, 151–160.

Cihlář, Z., Vojtová, L., Michlovská, L., Kučerík, J., 2016. Preparation and hydration characteristics of carbodiimide crosslinked lignite humic acids. Geoderma 274, 10–17. https://doi.org/10.1016/j.geoderma.2016.03.009.

Conte, P., 2019. Environmental applications of fast field cycling NMR relaxometry. In: Kimmich, R. (Ed.), Field-Cycling NMR Relaxometry: Instrumentation, Model Theories and Applications. RCS, pp. 229–254.

Conte, P., Nestle, N., 2015. Water dynamics in different biochar fraction. Magn. Reson. Chem. 53, 727–734.

de Jonge, H., Mittelmeijer-Hazeleger, M.C., 1996. Adsorption of CO2 and N2 on soil organic matter: nature of porosity, surface area, and diffusion mechanisms. Environ. Sci. Technol. 30, 408–413. https://doi.org/10.1021/es950043t.

Deshmukh, A.P., Simpson, A.J., Hadad, C.M., Hatcher, P.G., 2005. Insights into the structure of cutin and cutan from Agave Americana leaf cuticle using HRMAS NMR spectroscopy. Org. Geochem. 36, 1072–1085. https://doi.org/10.1016/j.orggeochem.2005.02.005.

Engemann, S., Reichert, H., Dosch, H., Bilgram, J., Honkimäki, V., Snigirev, A., 2004. Interfacial melting of ice in contact with SiO2. Phys. Rev. Lett. 92, 205701. https://doi.org/10.1103/PhysRevLett.92.205701.

Grün, A.Y., App, C.B., Breidenbach, A., Meier, J., Metreveli, G., Schaumann, G.E., Manz, W., 2018. Effects of low dose silver nanoparticle treatment on the structure and community composition of bacterial freshwater biofilms. PLoS One 13, e0199132. https://doi.org/10.1371/journal.pone.0199132.

Hu, W.-G., Mao, J., Xing, B., Schmidt-Rohr, K., 2000. Poly(methylene) crystallites in humic substances detected by nuclear magnetic resonance. Environ. Sci. Technol. 34, 530–534. https://doi.org/10.1021/es990506.

Jackson, M.T., Sampson, J., Prichard, H.M., 2007. Platinum and palladium variations through the urban environment: evidence from 11 sample types from Sheffield, UK. Sci. Total Environ. 385, 117–131. https://doi.org/10.1016/j.scitotenv.2007.06.004.

Jaeger, A., Schwarz, J., Kunhi Mouvenchery, Y., Schaumann, G.E., Bertmer, M., 2015. Physical long term regeneration dynamics of soil organic matter as followed by 1H solid-state NMR methods. Environ. Chem. https://doi.org/10.1071/EN14216 (doi:10.1071/EN14216).

Jäger, A., Schaumann, G.E., Bertmer, M., 2011. Optimized NMR spectroscopic strategy to characterize water dynamics in soil samples. Org. Geochem. 42, 917–925. https://doi.org/10.1016/j.orggeochem.2011.03.021.

Jäger, A., Bertmer, M., Schaumann, G.E., 2016. The relation of structural mobility and water sorption of soil organic matter studied by1H and13C solid-state NMR. Geoderma 284, 144–151. https://doi.org/10.1016/j.geoderma.2016.08.024.

Jancar, J., Hoy, R.S., Lesser, A.J., Jancarova, E., Zidek, J., 2013. Effect of particle size, temperature, and deformation rate on the plastic flow and strain hardening response of PMMA composites. Macromolecules 46, 9409–9426. https://doi.org/10.1021/ma400965c.

Komendova, R., Jezek, S., 2019. The distribution of platinum in the environment in large cities: a model study from Brno, Czech Republic. Int. J. Environ. Sci. Technol. 16, 3109–3116. https://doi.org/10.1007/s13762-018-1954-x.

Kučerík, J., Bursáková, P., Průšová, A., Grebíková, L., Schaumann, G.E., 2012. Hydration of humic and fulvic acids studied by DSC. J. Therm. Anal. Calorim. 110, 451–459. https://doi.org/10.1007/s10973-011-2178-1.

Kučerík, J., Schwarz, J., Jäger, A., Bertmer, M., Schaumann, G.E., 2014. Character of transitions causing the physicochemical aging of a sapric histosol. J. Therm. Anal. Calorim. 118, 1169–1182. https://doi.org/10.1007/s10973-014-3971-4.

Kučerík, J., Ondruch, P., Kunhi Mouvenchery, Y., Schaumann, G.E., 2018. Formation of water molecule bridges governs water sorption mechanisms in soil organic matter. Langmuir 34, 12174–12182. https://doi.org/10.1021/acs.langmuir.8b02270.

Kumahor, S.K., Hron, P., Metreveli, G., Schaumann, G.E., Vogel, H., 2015. Science of the total environment transport of citrate-coated silver nanoparticles in unsaturated sand. Sci. Total Environ. 535, 113–121. https://doi.org/10.1016/j.scitotenv.2015.03.023.

Kunhi Mouvenchery, Y., Jaeger, A., Aquino, A.J.A., Tunega, D., Diehl, D., Bertmer, M., Schaumann, G.E., 2013. Restructuring of a peat in interaction with multivalent cations: effect of cation type and aging time. PLoS One 8, e65359. https://doi.org/10.1371/journal.pone.0065359.

Kuznetsov, G.V., Piskunov, M.V., Volkov, R.S., Strizhak, P.A., 2018. Unsteady temperature fields of evaporating water droplets exposed to conductive, convective and radiative heating. Appl. Therm. Eng. 131, 340–355. https://doi.org/10.1016/j.applthermaleng.2017.12.021.

Majda, D., Bhattarai, A., Riikonen, J., Napruszewska, B.D., Zimowska, M., Michalik-Zym, A., Töyräs, J., Lehto, V.P., 2017. New approach for determining cartilage pore size distribution: NaCl-thermoporometry. Microporous Mesoporous Mater. 241, 238–245. https://doi.org/10.1016/j.micromeso.2017.01.005.

Makarieva, A.M., Gorshkov, V.G., Sheil, D., Nobre, A.D., Li, B.L., 2013. Where do winds come from? A new theory on how water vapor condensation influences atmospheric pressure and dynamics. Atmos. Chem. Phys. 13, 1039–1056. https://doi.org/10.5194/acp-13-1039-2013.

Michaelides, A., 2006. Density functional theory simulations of water–metal interfaces: waltzing waters, a novel 2D ice phase, and more. Appl. Phys. A Mater. Sci. Process. 85, 415–425.

Narvaez, J.A., Veydt, A.R., Wilkens, R.J., 2014. Evaluation of nanofluids as potential novel coolant for aircraft applications: the case of de-ionized water-based alumina nanofluids. J. Heat Transf. 136, 051702. https://doi.org/10.1115/1.4026216.

Navrotsky, A., 2003a. Materials and nanotechnology. J. Frankl. Inst. 340, 263–268. https://doi.org/10.1016/S0016-0032(03)00044-9.

Navrotsky, A., 2003b. Energetics of nanoparticle oxides: interplay between surface energy and polymorphism. Geochem. Trans. 4, 34–37. https://doi.org/10.1039/b308711e.

Ondruch, P., 2018. Soil Organic Matter Aging Processes and their Contribution to the Sequestration of Pollutants in Soil. University of Koblenz-Landau, Germany.

Ondruch, P., Jäger, A., Kucerik, J., Bertmer, M., Schaumann, G.E., 2017a. Influence of organic chemicals on aliphatic crystallites analyzed in whole soils. Geoderma 291, 40–46. https://doi.org/10.1016/j.geoderma.2016.12.016.

Ondruch, P., Kucerik, J., Steinmetz, Z., Schaumann, G.E., 2017b. Influence of organic chemicals on water molecule bridges in soil organic matter of a Sapric Histosol. J. Phys. Chem. A 121, 2367–2376. https://doi.org/10.1021/acs.jpca.6b10207.

Ondruch, P., Kučerík, J., Tunega, D., Silva, N.J., Aquino, A.J.A., Schaumann, G.E., 2019. Influence of water molecule bridges on sequestration of phenol in soil organic matter of sapric histosol. Environ. Chem. https://doi.org/10.1071/EN18137.

Philippe, A., Schaumann, G.E., 2014. Interactions of dissolved organic matter with natural and engineered inorganic colloids: a review. Environ. Sci. Technol. 48, 8946–8962. https://doi.org/10.1021/es502342r.

Philippe, A., Campos, D., Guigner, J.-M., Buchmann, C., Diehl, D., Schaumann, G., 2018. Characterization of the natural colloidal TiO2 background in soil. Separations 5, 50. https://doi.org/10.3390/separations5040050.

Pignatello, J.J., 1998. Soil organic matter as a nanoporous sorbent of organic pollutants. Adv. Colloid Interf. Sci. 76, 445–467. https://doi.org/10.1016/s0001-8686(98)00055-4.

Prichard, H.M., Fisher, P.C., 2012. Identification of platinum and palladium particles emitted from vehicles and dispersed into the surface environment. Environ. Sci. Technol. 46, 3149–3154. https://doi.org/10.1021/es203666h.

Prusova, A., Smejkalova, D., Chytil, M., Velebny, V., Kucerik, J., 2010. An alternative DSC approach to study hydration of hyaluronan. Carbohydr. Polym. 82, 498–503. https://doi.org/10.1016/j.carbpol.2010.05.022.

Pulit-Prociak, J., Banach, M., 2016. Silver nanoparticles - a material of the future…? Open Chem 14, 76–91. https://doi.org/10.1515/chem-2016-0005.

Rajput, V.D., Minkina, T., Sushkova, S., Tsitsuashvili, V., Mandzhieva, S., Gorovtsov, A., Nevidomskyaya, D., Gromakova, N., 2017. Effect of nanoparticles on crops and soil microbial communities. J. Soils Sediments, 2179–2187 https://doi.org/10.1007/s11368-017-1793-2.

Schaumann, G.E., 2005. Matrix relaxation and change of water state during hydration of peat. Colloids Surfaces A Physicochem. Eng. Asp. 265, 163–170. https://doi.org/10.1016/j.colsurfa.2005.02.040.

Schaumann, G.E., 2006. Soil organic matter beyond molecular structure part II: amorphous nature and physical aging. J. Plant Nutr. Soil Sci. 169, 157–167. https://doi.org/10.1002/jpln.200521791.

Schaumann, G.E., LeBoeuf, E.J., 2005. Glass transitions in peat - their relevance and the impact of water. Environ. Sci. Technol. 39, 800–806. https://doi.org/10.1021/es0490931.

Schaumann, G.E., Diehl, D., Bertmer, M., Jaeger, A., Conte, P., Alonzo, G., Bachmann, J., 2013. Combined proton NMR wideline and NMR relaxometry to study SOM-water interactions of cation-treated soils. J. Hydrol. Hydromechanics 61, 50–63. https://doi.org/10.2478/johh-2013-0007.

Seitz, F., Lüderwald, S., Rosenfeldt, R.R., Schulz, R., Bundschuh, M., 2015. Aging of TiO2 Nanoparticles Transiently Increases Their Toxicity to the Pelagic Microcrustacean *Daphnia magna*. https://doi.org/10.1371/journal.pone.0126021.

Šesták, J., Hubík, P., Mareš, J.J., 2010. Thermal analysis scheme aimed at better understanding of the Earth's climate changes due to the alternating irradiation. J. Therm. Anal. Calorim. 101, 567–575. https://doi.org/10.1007/s10973-010-0861-2.

Shrivastava, M., Srivastav, A., Gandhi, S., Rao, S., Roychoudhury, A., Kumar, A., Singhal, R.K., Jha, S.K., Singh, S.D., 2019. Monitoring of engineered nanoparticles in soil-plant system: a review. Environ. Nanotechnology, Monit. Manag. 11. https://doi.org/10.1016/j.enmm.2019.100218.

Theng, B.K.G., Yuan, G., 2008. Nanoparticles in the soil environment. Elements 4, 395–399. https://doi.org/10.2113/gselements.4.6.395.

Vitos, L., Ruban, A.V., Skriver, H.L., Kollár, J., 1998. The surface energy of metals. Surf. Sci. 411, 186–202. https://doi.org/10.1016/S0039-6028(98)00363-X.

Vojta, D., Vrankić, M., Bertmer, M., Schaumann, G.E., 2016. Dehydration of α-oxalic acid dihydrate: structural, spectroscopic and thermal study with implications on the disruption of water molecular bridges in soil organic matter. Thermochim. Acta 643, 73–82. https://doi.org/10.1016/j.tca.2016.09.019.

Volkov, R.S., Kuznetsov, G.V., Strizhak, P.A., 2015a. Experimental investigation of mixtures and foreign inclusions in water droplets influence on integral characteristics of their evaporation during motion through high-temperature gas area. Int. J. Therm. Sci. 88, 193–200. https://doi.org/10.1016/j.ijthermalsci.2014.10.002.

Volkov, R.S., Piskunov, M.V., Kuznetsov, G.V., Strizhak, P.A., 2015b. Water droplet with carbon particles moving through high-temperature gases. J. Heat Transf. 138, 014502. https://doi.org/10.1115/1.4031075.

Wiesmeier, M., Lützow, M. von, Wollschlaeger, U., Vogel, H.J., Garcia-Franco, N., Ließ, M., Urbanski, L., Hobley, E., Lang, B., Marin-Spiotta, E., Wesemael, B. van, Koegel-Knabner, I., von Lützow, M., Marin-Spiotta, E., van Wesemael, B., Rabot, E., Ließ, M., Garcia-Franco, N., Wollschläger, U., Vogel, H.J., Kögel-Knabner, I., 2019. Soil organic carbon storage as a key function of soils - a review of drivers and indicators at various scales. Geoderma 333, 149–162. https://doi.org/10.1016/j.geoderma.2018.07.026.

Wiesner, M.R., Lowry, G.V., Casman, E., Bertsch, P.M., Matson, C.W., Di Giulio, R.T., Liu, J., Hochella, M.F., 2011. Meditations on the ubiquity and mutability of nano-sized materials in the environment. ACS Nano 5, 8466–8470. https://doi.org/10.1021/nn204118p.

Xing, B., Vecitis, C.D., Senesi, N. (Eds.), 2016. Engineered Nanoparticles and the Environmentat. Biophysicochemical Processes and Toxicity, Wiley-IUPA. ed. John Wiley & Sons.

Xu, C., Peng, C., Sun, L., Zhang, S., Huang, H., Chen, Y., Shi, J., 2015. Distinctive effects of TiO2 and CuO nanoparticles on soil microbes and their community structures in flooded paddy soil. Soil Biol. Biochem. 86, 24–33. https://doi.org/10.1016/j.soilbio.2015.03.011.

Zhang, H., Gilbert, B., Huang, F., Banfield, J.F., 2003. Water-driven structure transformation in nanoparticles at room temperature. Nature 424, 1025.