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Elimination of interferences in determination of platinum and palladium in environmental samples by inductively coupled plasma mass spectrometry

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Abstract

Various approaches were evaluated in order to eliminate the spectral interferences noted when Pt and Pd has to be determined in environmental dust samples by ICP-MS. The chemical separation of Pt and Pd from the matrix components on ion-exchange resins was applied. The performance of cation-exchange resins (Dowex 50 WX-8, Dowex 50 WX-2, Dowex HCR-S, Varion KS, Cellex-P) for the separation of interfering ions was then examined. It was found that Dowex 50 WX-8 shows best performance. The effects of mass, mesh number of resin and concentration of Cl^- ions on matrix separation were also studied. Another approach was to use the anion-exchange sorbent Cellex-T, which allows almost total retention of both analytes followed by their elution with 0.1 $mol\,L^{-1}$ thiourea in 1 $mol\,L^{-1}$ HCl. This procedure however can be used only for platinum determination by ICP-MS. The accuracy of proposed procedures was confirmed by the analysis of certified material BCR-723, and then it was used for determination Pt and Pd in samples of road dust.

Keywords: Cation-exchanger; Anion-exchanger; Sample pre-treatment; Matrix separation; Road and tunnel dust

1. Introduction

The introduction of catalytic converters of automobiles containing platinum, palladium and rhodium (platinum group elements, PGEs) for reducing emission of gaseous pollutants, such as carbon monoxide, nitrogen oxides and hydrocarbons, has resulted in increasing concentration of PGEs in environmental matrices, especially in roadside dust, soil and plants [1,2]. The presence of Pt and Pd in such matrices can effect the human health and living organisms [3,4], therefore the investigation and control of PGEs content in environment are necessary.

The determination of Pt and Pd in complex matrices, such as environmental or biological samples is still a difficult task due to their extremely low concentrations and significant matrix effects. Most sensitive analytical methods, as graphite furnace atomic absorption spectrometry (GFAAS) [5–8], instrumental neutron activation analysis (INAA) [9], adsorptive stripping voltammetry (ASV) [10], inductively coupled plasma-optical emission spectrometry (ICP-OES) [11] and inductively coupled plasma-mass spectrometry (ICP-MS) [12–28] are commonly used for that purpose. Due to the very low detection limit and multielement capability of ICP-MS, this method is considered as the most appropriate for direct determination of PGEs in various environmental samples. Unfortunately, complex matrices of environmental samples are often a source of spectral and non-spectral interferences caused by monoatomic and polyatomic ions, formed in the plasma from the matrix constituents. Overlapping of interferent and analyte signals hampers obtaining accurate results.

The contribution of interferent in analyte signal depends on the concentration of both, the analyte and interferent as well as the ability of the formation of interfering species in the plasma. Mathematical correction, based on the evaluation of the contribution of interferent signal in that one for analyte, was successfully applied for elimination of spectral interferences occurring during determination of Pt by ICP-MS tech-

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nique [12–16], but was inefficient during determination of Pd [12,14–16]. Hence, the accurate results may be obtained only after chemical separation of Pt and Pd from the matrix. Among different separation techniques, solid phase extraction based on adsorption [17], ion-exchange [18–27] or chelating properties [28] of solid sorbents have been demonstrated to be most effective.

The ion-exchange methods exploit high affinity of Pt and Pd chlorocomplexes for anion-exchange resins and their low affinity for cation-exchange resins. The effective separation of Pt and Pd from the matrix of large amounts of base metals requires using large cation-exchange columns [18–21]. The other disadvantage of such procedures is partial retention of Pt and Pd on the column [29]. Because of low concentration of Pt and Pd in environmental samples, the application of anion-exchange resins seems to be preferred over the cation-exchange resins. However, the main limitation in using strong anion-exchangers is a non-selective retention of Pt and Pd chlorocomplexes on commercially available resins. Other elements that form anionic complexes (i.e. Al, Fe, Pb, Zn, Ni, Cu, Y) can be retained simultaneously with Pt and Pd, introducing spectral interference during detection step [11,22,30]. In some cases Pt and Pd are so strongly bound to the resin that for their quantitative recovery the use of high volumes (40–75 mL) of concentrated mineral acids [22–26] or total digestion of the resin [28,30] were proposed. In addition, when hot nitric acid was used for elution of Pd and Pt from AG 1-X8 resin the unexpected interferences were observed, probably due to partial digestion of the resin [22]. Some authors reported that in order to achieve accurate results for determination of Pt and Pd by ICP-MS, the combination of cation or anion exchange methods with isotope dilution technique (ID) was necessary [20,21,24,25].

To overcome these limitations we have evaluated and critically compared procedures based on different cation-exchanger and cellulose anion-exchanger for elimination of interferences during determination of Pt and Pd by ICP-MS. Cellulose sorbents are characterised by lower affinity to platinum group metals [5,6,31], what facilitates the elution process and in consequence assures the quantitative recovery of retained metals with small volume of eluents.

2. Experimental

2.1. Instrumentation

A quadrupole spectrometer (ICP-QMS) (ELAN 6100 DRC, Perkin-Elmer Sciex, USA) equipped with conventional Scott spray chamber and Meinhard nebulizer was used in this study. The working conditions of spectrometer were optimized daily in order to obtain the maximal sensitivity and stability as well as the lowest level of oxides and double charged ions. The operating conditions are given in Table 1. The isotopes ^{105}Pd and ^{195}Pt were used for quantification. The signals of other isotopes of analytes (^{104}Pd, ^{108}Pd, ^{194}Pt, ^{196}Pt) and interfering elements (^{65}Cu, ^{89}Y, ^{87}Sr, ^{179}Hf) were also monitored.

A PU 9100X (Philips Scientific, Cambridge, UK) atomic absorption spectrometer equipped with a PU 9390X electrothermal atomizer, FS-90 autosampler and deuterium background corrector was used for Pd and Pt determination during optimization of the separation procedures. The palladium and platinum hollow cathode lamps (CPI, USA) were operated at 8 and 10 mA current, respectively. The absorbance was measured in the peak height mode using pyrolytically coated graphite furnaces with 0.5 nm spectral bandpass at 247.6 nm for Pd and 265.9 nm for Pt. Sample aliquots of 20 μL volume were dispensed from autosampler cups into the graphite furnace. The following optimized time/temperature furnace programs for Pd and Pt determination were used: drying: 110 °C for 10 s, 160 °C for 10 s, ashing: 350 °C for 10 s, 1300 °C (Pd) or 1600 °C (Pt) for 5 s, atomization: 2400 °C (Pd) or 2700 °C (Pt) for 2.5 s.

Table 1
ICP-MS (ELAN 6100 DRC) operating conditions

Plasma	
RF power	1100 W
Frequency	40 MHz
Nebulizer gas flow rate (Ar)	0.93 mL min^{-1}
Plasma gas flow rate (Ar)	15.5 L min^{-1}
Auxiliary gas flow rate (Ar)	1.0 L min^{-1}
Data acquisition	
Mode	Electric scan
Dwell time	100 ms
Number of sweeps per reading	6
Number of replicates	3
Analytical masses	^{105}Pd, ^{195}Pt
Interfering ions	^{105}Pd: ^{40}Ar^{65}Cu$^+$, ^{89}Y^{16}O$^+$, ^{88}Sr^{16}OH$^+$, ^{88}Sr^{17}O$^+$; ^{195}Pt: ^{179}Hf^{16}O$^+$
Internal standard	^{115}In

Microwave system ETHOS PLUS (Milestone, Italy) was used for digestion of samples.

A solid-phase extraction system SPE-12G (Baker, Germany) equipped with cation-exchange columns and a system consisted of peristaltic pump Minipuls 3 (Gilson, France), PTFE tubing of i.d. 0.8 mm and anion-exchange columns were used for separation.

2.2. Reagents and materials

Concentrated HNO$_3$ (69%), HCl (37%) and HF (40%) (Suprapur, Merck) were used throughout this study. High-purity deionized water for the preparation of standards and sample solutions was obtained from Milli-Q system (Millipore, USA). Working solutions were prepared daily by dilution of stock solutions of 1000 mg L^{-1} of Pd and Pt (SPEX, Edison, NJ, USA) with high-purity water. Single-element stock solutions of Cu, Sr, Y, Hf, and In as internal standard (1000 mg L^{-1}, SPEX, Edison, NJ, USA) were used.

Thiourea (puriss p.a., Fluka, Germany) was used for elution of Pt and Pd from anion-exchange resin.

Cation-exchange resins: Dowex 50 WX-8 (Fluka, Germany), Dowex 50 WX-2, Dowex HCR-S (polystyrene matrix, sulfonic acid functional group; Dow Chemical Co, USA), Varion KS (styrene–divinylobenzene matrix, sulfonic acid functional group; Nitrokemia, Hungary) and Cellex-P (cellulose matrix, phosphonic acid functional group; Bio-Rad Laboratories, USA)