

Optimization of Determination of Platinum Group Elements in Airborne Particulate Matter by Inductively Coupled Plasma Mass Spectrometry

Marek Bujdoš,* Ingrid Hagarová, Peter Matúš,
Lucia Čanecká and Jana Kubová

Comenius University in Bratislava, Faculty of Natural Sciences, Geological Institute, 842 15 Bratislava, Slovakia

* Corresponding author: E-mail: bujdos@fns.uniba.sk

Received: 01-08-2011

Abstract

Determination of automotive traffic-emitted platinum group metals (PGM) by inductively coupled plasma quadrupole mass spectrometry (ICP-MS) was optimized. The interferences from Sr, Cu, Pb, Y, Cd, Zr and Hf were evaluated using model solutions. Plasma radiofrequency (RF) power and nebulizer gas flow were optimized for ^{103}Rh , ^{105}Pd , ^{108}Pd and ^{195}Pt . Two standard reference materials were analyzed: SARM-7 Platinum ore and BCR-723 Road dust. The optimized procedure was used to analyze samples of airborne particulate matter collected in the urban site with heavy automotive traffic in the centre of Bratislava, Slovakia.

Keywords: Airborne particulate matter, platinum group elements, inductively coupled plasma mass spectrometry

1. Introduction

Platinum group elements (PGEs) can be naturally found only at very low concentration in the earth crust. However, the use of PGEs in vehicle exhaust catalysts (VECs), in addition to some other applications, cause their anthropogenic emission and spread in the environment. PGE contamination initially occurs in airborne particulate matter (PM), roadside dust, soil, sludge and water, etc.; which finally results in bioaccumulation of these elements in the living organisms. The metallic form of these elements is generally considered to be inert as regards biological reactions. On the contrary, some of their compounds are very toxic and allergenic.^{1,2} The accurate determination of PGEs has been one of the difficult tasks in analytical chemistry because of their ultra-trace concentration in most geological, environmental and biological samples (typically 1–100 ng g⁻¹). The methods like electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) do not provide sufficient sensitivity and detection limits for the direct determination of these elements in such samples.³ Quadrupole ICP-MS is one of the most sensitive analytical techniques presently available for PGEs determination at trace levels generally having de-

tection limits in the order of ng g⁻¹. However, determination by quadrupole ICP-MS is hampered by spectral interferences from polyatomic ionic species, isobaric overlaps and doubly charged ions produced in the plasma from matrix constituents and suitable correction method must be developed and employed.^{4–7}

2. Experimental

2. 1. Airborne Particulate Matter Sampling

Sampling of the airborne particulate matter has been performed at the urban site, in the centre of Bratislava, Slovakia. Nitrocellulose membrane filters (Pragopor, Czech Republic) with pore size 1.2 μm and collection efficiency approximately 100% were used. Filters were changed every month in the time period between XII. 2009 and VI. 2010 and about 20–70 m³ of air was pumped through each sample.

2. 2. Certified Reference Materials

CRM SARM-7 (Platinum Ore, SA Bureau of Standards, Pretoria, South Africa) and BCR-723 (Road Dust, Institute for Reference Materials and Measurements, European Commission BCR)⁸ were used.

2. 3. Sample Treatment

All solutions were prepared using re-distilled water.

Nitric acid of 65% (Suprapur, Merck, Darmstadt, Germany) and hydrochloric acid of 30% (Suprapur, Merck, Darmstadt, Germany) were used for sample treatment.

CRM SARM-7 was digested on a hot plate in open PTFE vessels using mixture of HNO₃, HCl, HClO₄, H₂O₂ and HF.⁹ After digestion, the sample was evaporated to dryness and the residue was diluted in 1% HNO₃ and 2% HCl. The undissolved residue was removed from the digests by centrifugation (10 min at 3000 g).

CRM BCR-723 and airborne particulate matter on nitrocellulose membrane filters were digested in aqua regia (HNO₃ + HCl 1 mL + 3 mL) in PTFE beakers covered by watch glass overnight. Then another 1 mL of HNO₃ and 3 mL of HCl was added and the mixture was heated on sand bath for 5 hours. After the digestion, the samples were evaporated to the minimal volume of 1–2 mL, transferred to 25 mL volumetric flask and diluted in 1% HNO₃ and 2% HCl. The undissolved residue was removed from the digests by centrifugation (10 min at 3000 g).

The PGE calibration standards and the interferent model solutions were prepared from single element standard solutions (1.000 g L⁻¹, CertiPUR, Merck, Darmstadt, Germany)

All working solutions were prepared using 1% HNO₃ and 2% HCl addition.

2. 4. Instrumentation

The measurements were performed using a quadrupole ICP-MS spectrometer Perkin-Elmer Sciex Elan 6000 (without Dynamic Reaction Cell). The spectrometer was optimized to provide maximal intensity for Rh⁺. Ce-O⁺/Ce⁺ and Ba²⁺/Ba⁺ formation was kept under 2%. The optimized measurement conditions are shown in Table 1.

Table 1. ICP-MS operating conditions for the determination of PGMs

Sample introduction	
sample uptake	0.88 mL min ⁻¹
nebulizer type	cross-flow
nebulizer gas	argon, 0.9 L min ⁻¹
ICP	
RF power	1200 W
pulse stage voltage	1200 V
lens voltage	Auto Lens used
plasma gas	argon, 15 L min ⁻¹
auxiliary gas	argon, 1.2 L min ⁻¹
cones	nickel
Data acquisition	
acquisition mode	peak hopping
dwel time	50 ms
integration time	1000 ms

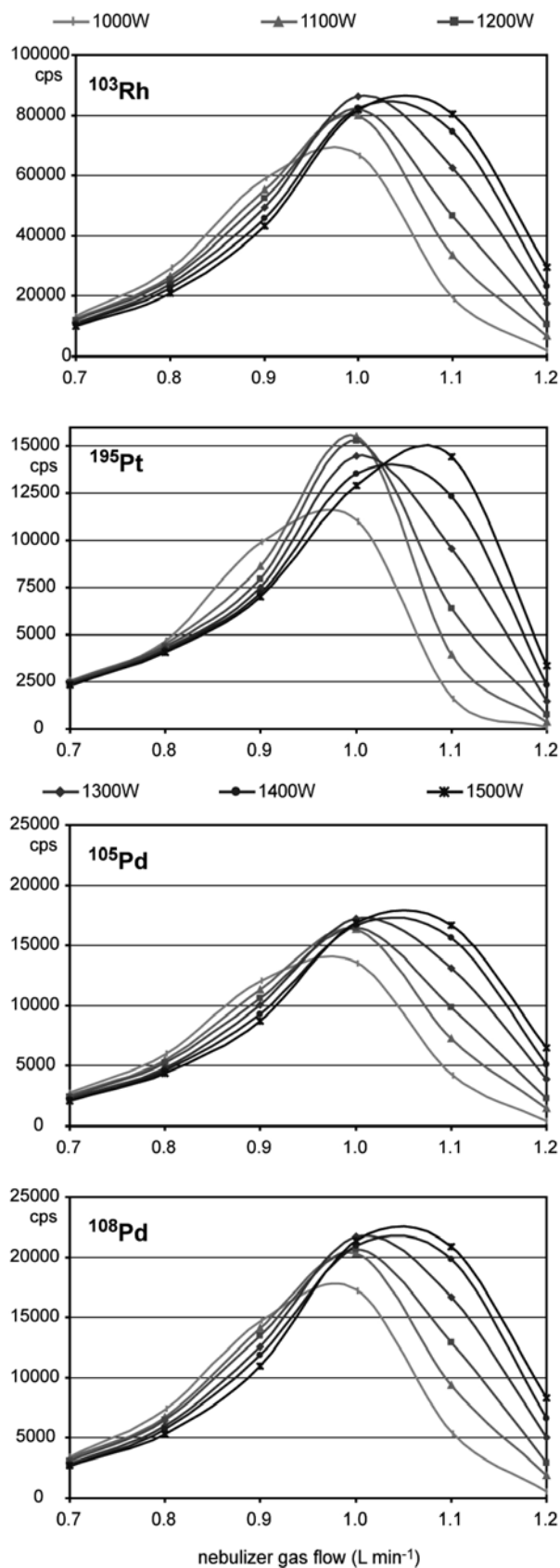


Figure 1. Optimization of plasma RF power and nebulizer gas flow for studied isotopes. Analyte concentration: 2 µg L⁻¹.

3. Results and Discussion

3.1. Optimization of Measurement of the Analytes on ICP-MS

The following isotopes were tested for the determination of PGMs: ^{103}Rh , ^{105}Pd , ^{108}Pd , and ^{195}Pt . The most important ICP-MS parameters, ICP RF power and nebulizer gas flow, were optimized for the best sensitivity and minimal formation of oxides and doubly charged ions. The concentration of analyte was $2\ \mu\text{g L}^{-1}$. The results of optimization experiments for these isotopes are shown in Fig. 1.

The highest sensitivities for analytes were achieved at nebulizer gas flows 1.0 and $1.1\ \text{L min}^{-1}$. The plasma power setting between $1100\ \text{W}$ and $1500\ \text{W}$ influenced the analyte signal at nebulizer gas flows under $1.0\ \text{L min}^{-1}$

slightly, however, at higher nebulizer gas flows the influence of RF power was considerable. An interference study was performed for further optimization.

3.2. Interference Study

The isobaric interferences from monoatomic and polyatomic ions produced in the plasma from matrix constituents are the most serious problem in the PGM determination using quadrupole ICP-MS without collision/reaction cell technology employment.^{6,7,10,11} The following interferences were studied in detail: SrO^+ , ArCu^+ and Pb^{2+} on $^{103}\text{Rh}^+$; YO^+ , ArCu^+ and SrOH^+ on $^{105}\text{Pd}^+$; Cd^+ and ZrO^+ on $^{108}\text{Pd}^+$ and HfO^+ on $^{195}\text{Pt}^+$.¹⁰ The solutions of PM digests were preliminary analyzed using ICP-MS for the content of these elements. The model solutions of

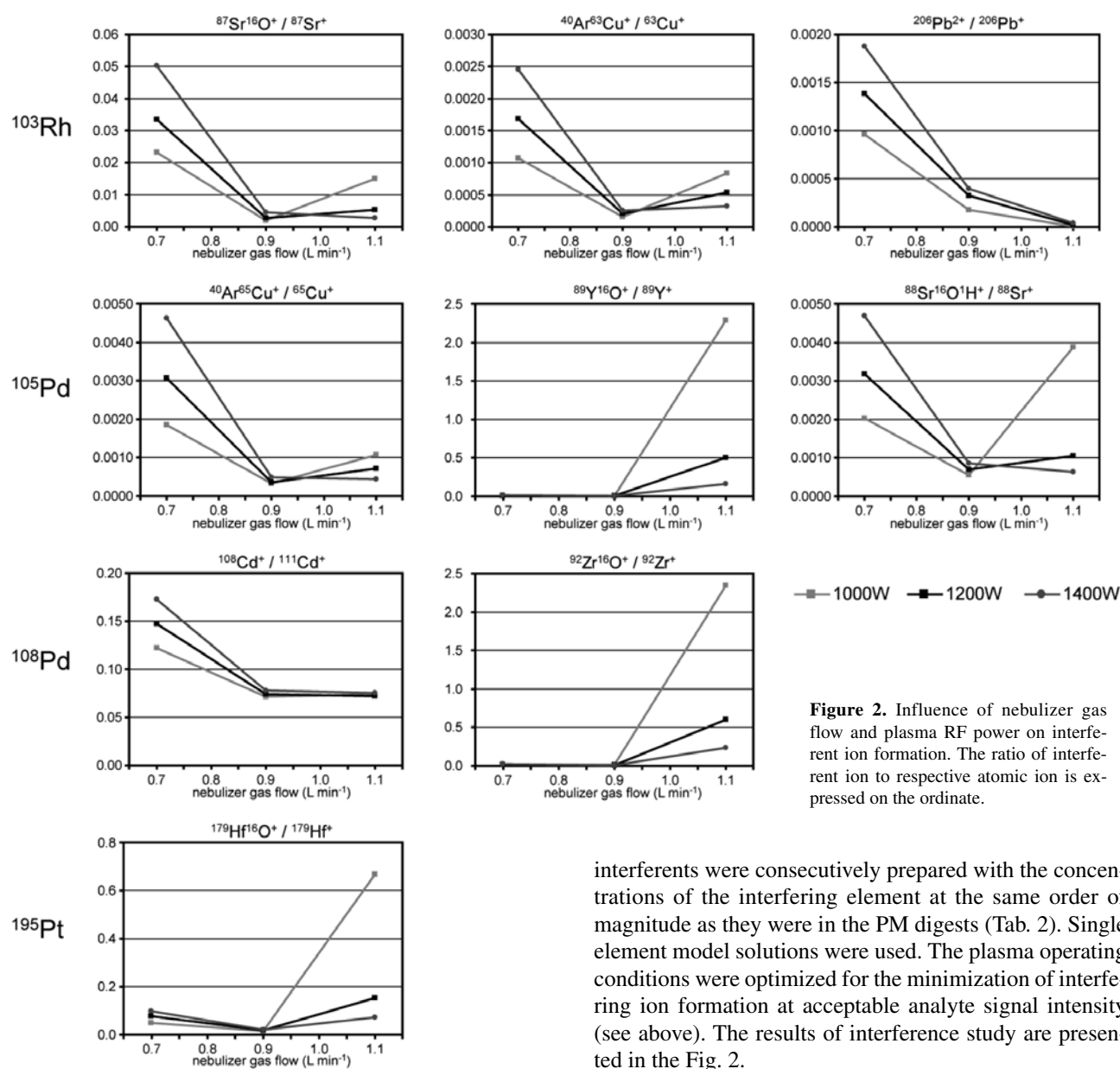


Figure 2. Influence of nebulizer gas flow and plasma RF power on interfering ion formation. The ratio of interfering ion to respective atomic ion is expressed on the ordinate.

interferents were consecutively prepared with the concentrations of the interfering element at the same order of magnitude as they were in the PM digests (Tab. 2). Single element model solutions were used. The plasma operating conditions were optimized for the minimization of interfering ion formation at acceptable analyte signal intensity (see above). The results of interference study are presented in the Fig. 2.

Table 2. Concentrations of potential interferences selected for the interference study

Element	Concentration $\mu\text{g L}^{-1}$
Pb	50
Cu	30
Sr	5
Zr	5
Y	2
Cd	2
Hf	1

The most interferences had minimal influence on the appropriate analytical mass of analytes at nebulizer gas flow of 0.9 L min^{-1} . If this gas flow is higher, mainly YO^+ , ZrO^+ and HfO^+ oxide formation drastically increases. Furthermore, the influence of the used RF power on the signal at nebulizer gas flow of 0.9 L min^{-1} is minor.

The best compromise between analyte signal intensity and acceptable oxides formation (under 2%) was found at nebulizer gas flow rate of 0.9 L min^{-1} at plasma RF power of 1200 W. The optimal conditions are listed in Tab. 1.

As a result of interference study a set of correction factors was calculated and used for the determination of PGM in the samples of airborne particulate matter. The values of correction factors are determined in model solutions with appropriate concentration of the interfering element (Tab. 2). They were calculated as the ratio of the signal measured on the m/z of individual platinum group metal to the signal measured on the m/z of the interferent while aspirating the appropriate model solution. They are summarized in Tab. 3.

Table 3. Mathematical coefficients used for the interference correction in airborne particulate matter

Analyte	Interferent ion / Monitored ion I. I. / M. I.	Correction factor I. I. / M. I.
^{195}Pt	$^{179}\text{Hf}^{16}\text{O}^+ / ^{179}\text{Hf}^+$	0.017331
^{108}Pd	$^{108}\text{Cd}^+ / ^{111}\text{Cd}^+$	0.074149
	$^{92}\text{Zr}^{16}\text{O}^+ / ^{92}\text{Zr}^+$	0.011320
^{105}Pd	$^{40}\text{Ar}^{65}\text{Cu}^+ / ^{65}\text{Cu}^+$	0.000357
	$^{89}\text{Y}^{16}\text{O}^+ / ^{89}\text{Y}^+$	0.006138
	$^{88}\text{Sr}^{16}\text{O}^+\text{H}^+ / ^{88}\text{Sr}^+$	0.000692
^{103}Rh	$^{87}\text{Sr}^{16}\text{O}^+ / ^{87}\text{Sr}^+$	0.002738
	$^{40}\text{Ar}^{63}\text{Cu}^+ / ^{63}\text{Cu}^+$	0.000203
	$^{206}\text{Pb}^{2+} / ^{206}\text{Pb}^+$	0.000324

3.3. Analysis of CRM and Samples of Airborne Particulate Matter

The optimized procedure was used for the determination of platinum group elements in the certified reference materials SARM-7 and BCR-723. The results are shown in the Tab. 4.

Table 4. Determination of Pt, Pd and Rh in the certified reference materials SARM-7 and BCR-723

Analyte	Certified ng g^{-1}	Measured ng g^{-1}	Recovery %
CRM SARM-7			
Pt	3740 ± 45	3580 ± 130^a	95.7
Pd	1530 ± 32	1490 ± 30	97.4
Rh	240 ± 13	221 ± 15	92.1
CRM BCR-723			
Pt	81.3 ± 2.45	75.1 ± 3.48	92.4
Pd	6.0 ± 1.83	N.D. ^b	N.D.
Rh	12.8 ± 1.22	10.4 ± 1.85	81.3

^a Values expressed as average \pm S.D. ($n = 4$).

^b Not determined.

The results of analysis of CRM SARM-7 are in good agreement with the certified values. The content of PGM in this reference material is relatively high, therefore the determination of all three elements was possible using all investigated isotopes (^{103}Rh , ^{105}Pd , ^{108}Pd and ^{195}Pt). Use of ^{195}Pt and ^{103}Rh isotopes and the mathematical corrections enabled the determination of Pt and Rh in the CRM BCR-723 and airborne particulate matter from Bratislava, Slovakia. The determination of Pd was not possible due to the interference of Zr, Sr and Y. The content of these interferences in the samples is very high and mathematical corrections are not able to correct the measured signals reliably. The results are summarized in Tab. 5.

Table 5. Determination of Pt, Pd and Rh in the airborne particulate matter from Bratislava, Slovakia

Sample collection month / year	Pt pg m^{-3}	Pd pg m^{-3}	Rh pg m^{-3}
XII / 2009	5.3 ± 0.5^a	N.D. ^b	1.2 ± 0.2
I / 2010	11.4 ± 0.8	N.D.	2.1 ± 0.3
II / 2010	3.2 ± 0.4	N.D.	1.5 ± 0.2
IV / 2010	8.9 ± 0.7	N.D.	5.5 ± 0.6
V / 2010	14.4 ± 1.1	N.D.	8.0 ± 0.8
VI / 2010	18.6 ± 1.5	N.D.	11.7 ± 0.7

^a Values expressed as average \pm S.D. ($n = 4$).

^b Not determined.

4. Conclusions

A simple method for analysis of PGMs in airborne particulate matter and geological samples using hot plate aqua regia digestion and quadrupole ICP-MS determination was proposed. Conditions for platinum group metal determination were optimized, the most important interferences were investigated. The platinum group metals were determined in CRM SARM-7, CRM BCR-723 and airborne particulate matter from Bratislava, Slovakia. Deter-

mination of PGM in CRM SARM-7 was possible using all studied isotopes (^{103}Rh , ^{105}Pd , ^{108}Pd and ^{195}Pt) employing mathematical correction equations. In CRM BCR-723 and airborne particulate matter the determination of Pt and Rh was possible using mathematical corrections. However, the determination of Pd was not possible neither using ^{105}Pd nor ^{108}Pd isotope due to the strong matrix interferences (predominately caused by Zr, Sr and Y oxide formation) which were not reliably correctable using mathematical equations.

5. Acknowledgements

The work was supported by the Science and Technology Assistance Agency under the contract No. LPP-0188-06, LPP-0038-06 and the Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences under the contracts No. VEGA 1/0639/11, VEGA 1/0257/10, and VEGA 1/0860/11.

Povzetek

Optimizirali smo določevanje kovin iz platinske skupine (PGM) v avtomobilskih izpušnih plinih z uporabo masne spektrometrije z induktivno sklopljeno plazmo (ICP-MS). Interference, ki izhajajo iz Sr, Cu, Pb, Y, Cd, Zr in Hf smo ovrednotili z uporabo modelnih raztopin. Radiofrekvenčno (RF) moč plazme in tok razpršilnega plina smo optimizirali za ^{103}Rh , ^{105}Pd , ^{108}Pd in ^{195}Pt . Analizirali smo dva standardna referenčna materiala: SARM-7 platinsko rudo in BCR-723 cestni prah. Optimiziran postopek smo uporabili za analizo delcev iz zraka po vzorčenju v mestnem središču Bratislave na Slovaškem, kjer je gost mestni promet.

6. References

1. L. Sikorová, R. Ličbinský, V. Adamec, *Chem. Listy* **2011**, *105*, 361–366.
2. C. L. S. Wiseman, F. Zereini, *Sci. Total Environ.* **2009**, *407*, 2493–2500.
3. P. Petrova, S. Velichkov, N. Velitchkova, I. Havezov, N. Daskalova, *Spectrochim. Acta Part B* **2010**, *65*, 130–136.
4. K. Ravindra, L. Bencs, R. Van Grieken, *Sci. Total Environ.* **2004**, *318*, 1–43.
5. L. Bencs, K. Ravindra, R. Van Grieken, *Spectrochim. Acta Part B* **2003**, *58*, 1723–1755.
6. M. Krachler, A. Alimonti, F. Petrucci, K. J. Irgolic, F. Forastiere, S. Caroli, *Anal. Chim. Acta* **1998**, *363*, 1–10.
7. R. Djingova, H. Heidenreich, P. Kovacheva, B. Markert, *Anal. Chim. Acta* **2003**, *489*, 245–251.
8. R. A. Sutherland, *Anal. Chim. Acta* **2007**, *582*, 201–207.
9. J. Medved', V. Streško, J. Kubová, J. Polakovičová, *Fresenius J. Anal. Chem.* **1998**, *360*, 219–224.
10. M. B. Gomez, M. M. Gomez, M. A. Palacios, *Anal. Chim. Acta* **2000**, *404*, 285–294.
11. K. Simitchiev, V. Stefanova, V. Kmetov, G. Andreev, A. Sanchez, A. Canals, *Talanta* **2008**, *77*, 889–896.
12. R. Djingova, H. Heidenreich, P. Kovacheva, B. Markert, *Anal. Chim. Acta* **2003**, *489*, 245–251.