

A PRELIMINARY STUDIES FOR THE DETERMINATION OF PLATINUM GROUP ELEMENTS, PGEs, IN ROAD DUST FROM SÃO PAULO CITY USING A QUADRUPOLE-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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ABSTRACT

This paper describes the main parameters involved in the platinum group elements (PGEs) determination by ICP-MS, interfering elements separation by the cation-exchange procedure after two digestion procedures. The eluent volume and choice of isotopes for ICP-MS determination was evaluated by elution curve of the cation-exchange technique using Dowex 50WX8, 200-400 mesh resin and a certified reference materials, BCR-723 (road dust). Analytical results and instrumental methods for analysis of platinum group elements were evaluated by ultrasound assisted extraction and microwave-assisted digestion. Two certified reference materials for the determination of PGEs in used auto catalysts (SRM 2556 and SRM 2557), were used for this evaluation. The main advantage of microwave-assisted digestion over ultrasound-assisted extraction was better recoveries for Rh (92% and 66%, respectively). Pt and Pd had almost the same recoveries (105% and 104%, for Pt, respectively and 89% and 83% for Pd). Therefore, the microwave-assisted digestion was chosen for this purpose.

1. INTRODUCTION

In Brazil, since 1992, gasoline and flex vehicles has been equipped with a three-way catalytic converter (WTC), which use small amounts of three platinum group elements (PGEs); platinum (Pt), palladium (Pd) and rhodium (Rh). Pt and Pd oxidize unburned hydrocarbons and CO to CO₂, while Pt and Rh reduce nitrogen oxidize (NO₂ and NO) to N₂ [1].

This catalytic converter has experienced the effects of high temperatures and severe vibration during operation of the vehicle, causing abrasion, attrition and release PGEs particles to the environment [2]. The PGE can be allergenic and / or carcinogenic species when inhaled by humans as particulate matter. Road dust in vehicle traffic routes consist of atmospheric deposition, soil erosion (weathering), resuspension and anthropogenic material [3]. During the last decade road dust has been used as an important environment monitor to PGEs contamination.

ICP-MS is the only technique for routine PGEs determination in environmental samples as road dust samples, at ultra traces levels.[4]. However, to obtain reliable results for PGEs, matrix separation, after digestion and evaporation, is necessary to eliminate mass interferences due to the matrix components. This procedure is necessary to eliminate or reduce spectral interferences, the plasma gas ⁴⁰Ar, for instance, combine with ⁶³Cu, ⁶⁵Cu, and ⁶⁶Zn to spectrally overlap ¹⁰³Rh, ¹⁰⁵Pd and ¹⁰⁶Pd respectively. Also doubly-charged ²⁰⁶Pb²⁺⁺ significantly interferes with ¹⁰³Rh [4]. Additionally, Pd is subject to polyatomic interferences

from oxides, YO^+ , MoO^+ , ZrO^+ and Rh from RbO^+ , SrO^+ and Hf isotopes interfere in Pt determination by HfO^+ [4].

The interfering species can be chemically removed by tellurium coprecipitation method [4] or by ion-exchange methods in HCl medium [5].

The objectives of this study were to discuss the main parameters involved in the platinum group elements, PGEs, determination by ICP-MS. These parameters were evaluated after ultrasound assisted extraction and microwave-assisted digestion and Elements and polyatomic interferences separation by the cation-exchange resin. Two certified reference materials, "Used Catlitic" (SRM 2556 and SRM 2557), were used for method validation.

2. EXPERIMENTAL

2.1. Reagents and materials

Hydrochloric and Nitric acids (Merck) were used, and further purified by sub-boiling distillation in quartz equipment.

A cation-exchange resin (Dowex 50WX8 200-400 mesh, Sigma-Aldrich, Saint Louis, MO) was used to chemically separate PGEs from the sample matrices. The resin was contained in 12 mL Poly-Prep chromatography columns (2 mL bed volume with 10 mL reservoir, Bio-Rad Laboratories Inc., Hercules, CA).

^{115}In was used as internal standards for ^{105}Pd and ^{103}Rh and ^{195}Pt determination to correct for instrumental drift or non-spectral interferences because of their low abundance in road dust, similar atomic mass, and broadly similar chemical and physical properties to those of the PGEs.

The standard reference materials used consisted of "Used Catlitic" (SRM 2556 and SRM 2557), in powder form, National Institute of Standards and Technology) with a certified content of Pt, Pd and Rh.

2.2. Instrumentation

Methodology and Sample digestions for ICP-MS analysis

2.2.1. Microwave-assisted acid digestion procedure

The samples were digested using the procedure similar to Spada [5]: Digestions of samples were performed in a programmable 1030 -1800 W microwave system (MARS 6, CEM Corp., Matthews, NC) using Xpress 55 mL Teflon vessels rated at 200 °C. Conditions inside the vessels were monitored and controlled in every vessel with an infrared sensor.

Each sample (200 mg for BCR 723-road dust, 100 mg for SRMs 2556 and 2557) were accurately weighted in Xpress 55 mL Teflon vessels to which 8 mL of *acqua regia* were added and left for 5 min and loosely capped. The control points were 200 °C and 300 psig with a ramp time of 20 min. and dwell time of 20 min. After digestions in aqua regia, of sample were taken to in 50-mL centrifuge tubes and diluted in H_2O ultrapure to 20 and 40 mL to BCR and SRMs respectively. Sub samples were evaporated almost to dryness on hot plate

at ~80°C in a Teflon Becker. The resulting residues were dissolved in 2 mL of concentrated HCl and heated again to almost dryness. This treatment was repeated twice more to remove satisfactorily HNO₃. The final residues were dissolved in 15 mL 0.5M HCl prior cation exchange.

2.2.2. Ultrasound assisted acid extraction procedure

Each sample (200 mg for BCR 723-road dust, 100 mg for SRMs 2556 and 2557) were accurately weighted in 50-mL centrifuge tubes adding 8 mL of aqua regia. The tubes were warmed in an ultrasonic bath at 65°C for 35 min. using the procedure similar to Ribeiro [6]. Samples were centrifuged (t=10 min and Rpm=3,000). The solutions obtained were transferred to another 50-mL centrifuge tubes and diluted in H₂O ultrapure to 20 and 40 mL to BCR and SRMs respectively. Sub samples were evaporated almost to dryness on hot plate at ~80°C in a Teflon Becker. The resulting residues were dissolved in 2 mL of concentrated HCl and heated again to almost dryness. This treatment was repeated twice more to remove satisfactorily HNO₃. The final residues were dissolved in 15 mL 0.5M HCl prior cation exchange.

2.2.3. Separation on cation-exchange resin

The interferente species can be chemically removed by cation-exchange resin. Before each use, Dowex 50WX8, 200-400 mesh resin was cleaned using the procedure similar to Spada. [5] Each Poly-Prep column was prepared with 3.5 mL of cleaned resin in 0.5M HCl. The resin was first equilibrated with 10 mL of 0.5M HCl and the eluent was collected in a polyethylene tube used as the column background sample. Then, this tube is replaced with a sample tube and 5 mL of sample in 0.5M HCl were added to the column. The eluent was collected at a flow of 0.2 mL min⁻¹. After the samples passed through the column, the resin was rinsed by adding 3 mL 0.5M HCl, collected in the same tube.

2.2.4. Analysis by ICP-QMS

A Nexion 300D ICP-Mass Instrument was used for PGEs determination. Pt, Pd and Rh were quantified. For the polyisotopic elements Pt and Pd, at least three isotopes were monitored to be compared with values reported in reference materials. Then, the isotope with the least isobaric or polyatomic interferences was used.

Daily optimization was performed using a 1µg L⁻¹ NexIon Setup solution (PerkinElmer), consisting of Be, Ce, Fe, In, Li, Mg, Pb, and U in 1% HNO₃. Formation of oxides (¹⁵⁶CeO⁺ / ¹⁴⁰Ce+ < = 0,035) and doubly charged ions (⁷⁰Ce⁺⁺ / ¹⁴⁰Ce < = 0.035) was minimized by adjusting nebulizer gas flow. Auto lens voltage was adjusted to maximize ion transmission based on ⁹Be > 3000, ²⁴Mg >20000, ¹¹⁴In>50000, and ²³⁸U>40000 cps. Under typical operating conditions, sensitivities for ⁹Be, ²⁴Mg, ¹¹⁵In, and ²³⁸U were approximately 9000, 70000, 70000, and 40100 cps, respectively. Calibration was performed with multi-element standards contained Pt, Pd and Rh and interfering elements (Y, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Pb, and Hf) were also monitored.

Nickel cones were cleaned using abrasive “Silver”, detergent and 2% HNO₃ by ultrasonication for 5min approximately once every 60 samples or when ¹¹⁵In sensitivity was decreased by ~25%.

2.2.5. Elution curve of the cation-exchange technique and results of PGEs determination

Eluent volume and choice of isotopes for ICP-MS determination was evaluated by elution curve of the cation-exchange technique, Dowex 50WX8, 200-400 mesh resin, using a synthetic standard based in elements concentrations from the certified reference materials, BCR-723 (road dust).

Separation of PGEs from other interfering elements were done with interfering elements form weaker anion complexes or stables cationic species with retention in a cationic resin, as far as PGEs were not retained in under these conditions 0.5M Hydrochloric acid medium, is due to the formation of highly stable anionic cloro-complexes [5, 7].

In order to confirm the immediate elution of PGEs, the standard solution containing known amount of PGEs and interfering elements in similar concentrations as BCR 723 (road Dust) was prepared and its elution behavior on Dowex resin was investigated. These test standard solution was loaded on the columns and was eluted with 11mL 0.5M HCl. The aliquots (1 mL) were collected separately and the PGEs contents were analyzed by ICP-MS. The elution curves of the PGEs are showed in Fig. 1.

The Fig.1 showed the efficient separation of interferences spectral to four Pt isotopes and ^{103}Rh with the elution 7 mL 0.5M HCl. Therefore, only ^{105}Pd showed an effective separation to spectral interferences, evidenced only by the concentration of the Pd using ^{105}Pd isotope, in the certified reference materials, road dust (BCR-723), was recovered in the range 80 - 90%.

This efficient separation of interferences spectral was also monitored by measurements of isotopes ratio values, Table 1.

Table 1: The isotopes ratio values between natural abundance and three certified reference materials.

Ratio	Natural Abundance	Ultrasound extraction			Microwave digestion		
		SRM		BCR	SRM		BCR
		2556	2557		2556	2557	
$^{194}\text{Pt}/^{195}\text{Pt}$	0.97	0.98	0.98	0.98	0.98	0.97	0.98
$^{194}\text{Pt}/^{196}\text{Pt}$	1.30	1.31	1.30	1.21	1.29	1.29	1.25
$^{195}\text{Pt}/^{196}\text{Pt}$	1.34	1.33	1.33	1.23	1.32	1.33	1.27
$^{194}\text{Pt}/^{198}\text{Pt}$	4.57	4.15	4.35	0.14	4.23	4.39	0.19
$^{105}\text{Pd}/^{106}\text{Pd}$	0.82	0.82	0.83	0.04	0.82	0.81	0.05
$^{105}\text{Pd}/^{108}\text{Pd}$	0.84	0.83	0.82	0.05	0.84	0.82	0.05

Table 1 shows that similar ratio between the natural abundance value and isotope ratio measurements from two certified reference materials, Used Auto catalyst (SRM 2556 and SRM 2557). Therefore, the road dust, (BCR-723) showed differences between the natural abundance value and the $^{194}\text{Pt}/^{198}\text{Pt}$, $^{105}\text{Pd}/^{106}\text{Pd}$ and $^{105}\text{Pd}/^{108}\text{Pd}$ ratios. These results showed the non efficient separation of interferences spectral for this certified reference materials. The contribution of these isobaric mass interferences to the Pd isotopes can be to correct mathematically after cation exchange resin procedure [4].

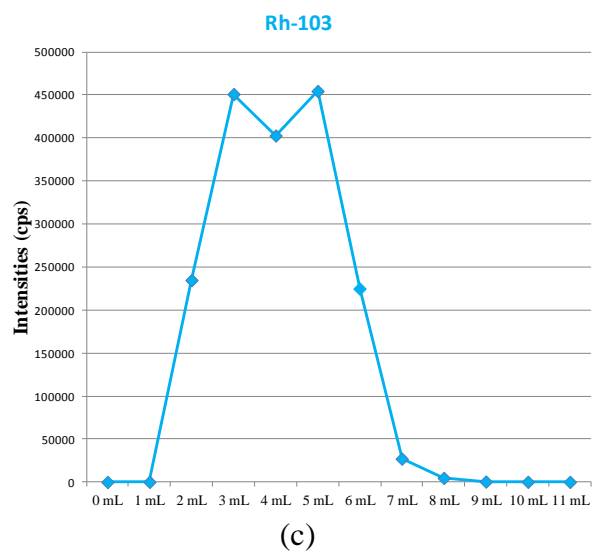
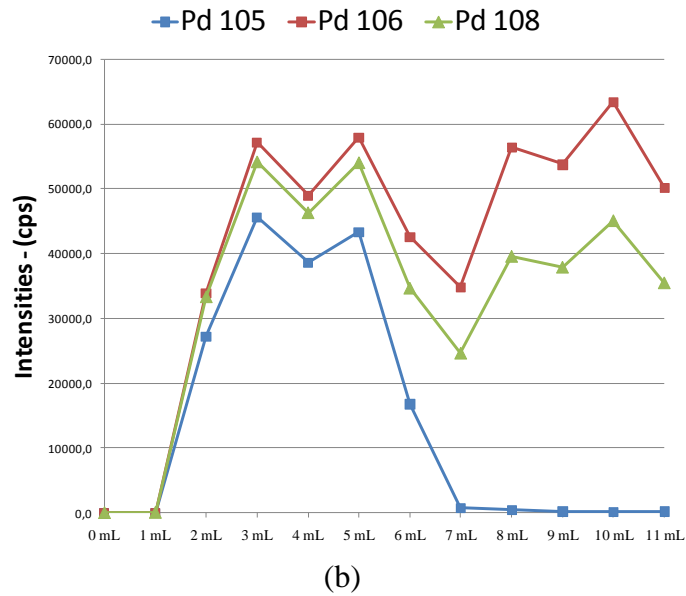
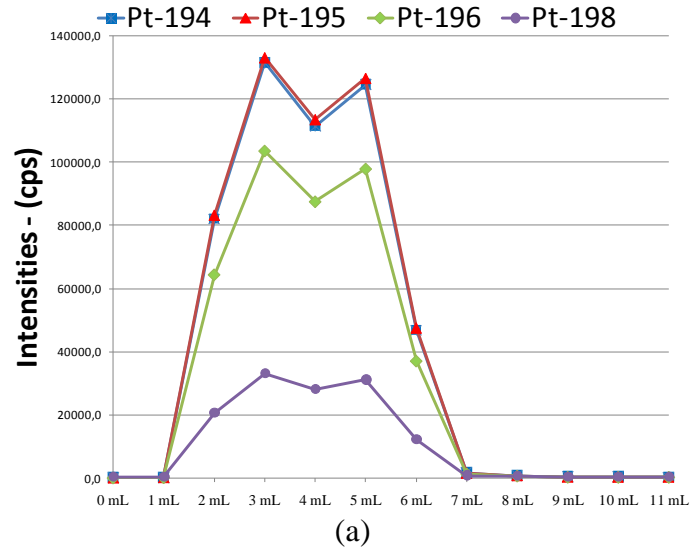


Figure 1: Elution curves of Pt(a), Pd(b) and Rh(c). Flow rate: 0.2 mL min⁻¹, 0.5 M HCl medium.

In order to evaluate the chemical and instrumental methods for analysis of platinum group by ICP-MS technique, the analysis of two certified reference materials, Used Auto catalyst (SRM 2556 and SRM 2557), were used. From the obtained results (Table 2) it is evident that separation of interfering ions by cation-exchange resin from samples leached with aqua regia was effective, also due to the fact that the elements analyzed by different isotopes showed the same concentration to the total concentration of element. These results were confirmed by maintenance of natural isotope ratio value (Table 1).

It was also found that the microwave-assisted acid digestion procedure was more effective than ultrasound assisted acid extraction procedure, due the best recovery of Rh.

Table 2: The content of Pt, Pd and Rh in used catalytic (SRM 2556 and SRM 2557) after aqua regia digestion using two digestion procedure (Microwave x Ultrasound)

Digestion	Ultrasound		Microwave		Certified Value
Isotope analyzed	$\mu\text{g g}^{-1}$ a	Recovery %	$\mu\text{g g}^{-1}$ a	Recovery %	SRM 2556 $\mu\text{g g}^{-1}$
^{194}Pt	722.9 ± 5.4	104	734.4 ± 0.5	105	697.4 ± 2.3
^{195}Pt	715.5 ± 7.8	103	731.5 ± 8.2	105	
^{196}Pt	713 ± 11	102	735.0 ± 6.4	105	
^{198}Pt	744.4 ± 8.7	107	736 ± 13	106	
^{103}Rh	33.8 ± 0.4	66	47.3 ± 0.8	92.4	51.2 ± 0.5
^{105}Pd	271.8 ± 3.1	83	288.6 ± 3.7	89	326.0 ± 1.6
^{106}Pd	267.9 ± 2.0	82	283.4 ± 2.4	87	
^{108}Pd	237.8 ± 1.8	73	251.2 ± 2.1	77	
					SRM 2557
^{194}Pt	1108 ± 13	98	1235 ± 13	109	1131 ± 11
^{195}Pt	1102 ± 6	97	1241 ± 16	110	
^{196}Pt	1104 ± 15	98	1238 ± 16	109	
^{198}Pt	1101 ± 12	97	1218 ± 13	108	
^{103}Rh	84.3 ± 0.8	62.4	127.2 ± 1.1	94.1	135.1 ± 1.9
^{105}Pd	190.4 ± 1.3	82	208.5 ± 2.7	90	233.2 ± 19
^{106}Pd	186.4 ± 3.3	80	208.8 ± 3.5	90	
^{108}Pd	168.5 ± 3.3	73	185.9 ± 1.9	80	

^a The results express the total concentration of element analyzed and not the isotopic concentration.

2.2.6. Blank samples and detection limits

The detection limits for this method was established in agreement to INMETRO [8]. Seven blank samples were prepared following the same procedure for the two certified reference materials. The seven blank samples were spiked with $0.2 \mu\text{g g}^{-1}$ of Pt, Pd and Rh. The detection limits obtained were 0.15 , 0.16 and $0.18 \mu\text{g g}^{-1}$ for Pt, Rh and Pd respectively.

3. CONCLUSIONS

The main advantage of microwave-assisted acid digestion procedure over ultrasound- assisted extraction was the better recovery to ^{103}Rh . Therefore, the microwave digestion was chosen in order to avoid loss of rhodium recovery.

The concentration of the platinum group elements, excluding ^{108}Pd isotope, in the two certified reference materials, used auto catalyst (SRM 2556 and SRM 2557), after the microwave-assisted acid digestion and cation resin procedure, were recovered in the range 87 -110%. Therefore, the cation exchange procedure used to eliminate or reduce spectral interferences in PGEs analysis by ICP-Ms was efficient to this propose.

Therefore, further studies with isotope dilution (ID) are required in order to evaluate the concentration of Pd and Pt isotopes by ID-ICP-MS, isotope dilution inductively coupled plasma-mass spectrometry, which is considered the most accurate analytical method and regarded as definitive method.

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