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Multi-element determination of Pt, Pd and Ir traces in environmental samples by ICP-MS after pre-concentration

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ABSTRACT

An automated flow analysis method with on-line column pre-concentration/ inductively coupled plasma mass spectrometry (ICP-MS) was developed for the simultaneous determination of Pt, Pd and Ir in environmental samples. The system is based on retention of the analytes onto a column filled with 1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide immobilized on an aminopropyl-controlled pore glass (PSTH-cpg) placed in the injection valve of a simple flow manifold. The retained platinum group metals (PGMs) were subsequently eluted with a mixture of HNO_3 and thiourea. The effects of chemicals and flow variables were investigated. The optimized operating conditions were: sample pH 3.2, sample flow rate: 1.1 mL min^{-1}; eluent flow rate: 2.1 mL min^{-1} and eluent 0.03% m/v thiourea solution in 3.2% (v/v) HNO_3. The detection limits obtained were 78.5 ng L^{-1} for Pt, 55.5 ng L^{-1} for Pd and 0.1 ng L^{-1} for Ir. The enrichment factors were 18, 2.3 and 43 for Pt, Pd and Ir, respectively. The accuracy of the method was checked by the analysis of certified reference materials and by determining the analytes content in spiked environmental samples. Recovery was found to be in the range 93–107% in all cases.

1. Introduction

The platinum group metals (PGMs) are nowadays being emitted to an increasing extend into the environment. Traditional emission sources of PGMs are the mining and smelting industries [1]. However these elements are worldwide applied in vehicles and some household utensils, to reduce the emissions of gaseous pollutants such as carbon monoxide, nitrogen oxides and hydrocarbons. Mostly, Pt, Pd and Rh contained in vehicle exhaust catalyst (VECs) were introduced in the middle 1970s (USA-1975, Germany-1984, EU-1993). Platinum has been used as a catalytic converter material for the refinement of automobile exhaust gases. Thus, an increasing number of cars equipped with catalytic converters have these novel anthropogenic metals [2,3]. Although the benefits of car catalysts are indisputable, highly toxic elements including Pt, Rh and Pd are released into the atmosphere. The release of these PGMs is found to increase the levels of contamination in environmental matrices, especially in soils, plants and road sediments [4] as well as in airborne particles [5]. Platinum content of road dusts can be soluble, and it enters the waters, sediments, soil and finally, the food chain [6]. The metallic form of these elements is generally considered to be inert as regards biological reactions. However, some Pt salts (especially those containing chloride) are toxic, cytotoxic and allergenic. PGMs have also been associated with asthma, nausea, increased hair loss, increased spontaneous abortion, dermatitis and other serious health problems in humans [7]. There is therefore a growing concern over human health and environmental risks resulting from the increasing concentrations of PGMs in the environment. The development of analytical methods for the determination of trace amounts of PGMs in water solutions, soils, sediments and biological matrices is important not only for the pollution control of the environment but also as a first step in the development of techniques for the recovery of PGMs from waste materials [8].

The accurate determination of these elements in environmental samples, such as soils, sediments and waters is still a difficult task due to their extremely low concentrations and significant matrix effects. Due to the very low detection limits and multi-element capability of inductively coupled plasma-mass spectrometry (ICP-MS), this technique is considered as the most appropriate for the determination of PGMs in these samples [9]. However, direct aspiration of environmental samples, e.g. sea water, into the plasma are often a source of spectral (“overlap” or “mass”) and no-spectral (matrix) interferences caused by monoatomic and polyatomic ions, formed in the plasma from matrix

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Table 1
ICP-MS operating conditions.

Instrument	Elan DRC-e (Perkin-Elmer)
Nebulizer gas flow rate (L min^{-1})	Ar 0.90–0.98
Auxiliary gas flow rate (L min^{-1})	1.2
Plasma gas flow rate (L min^{-1})	15
Autolens voltage (V)	6.75–8.75
Incident power (kW)	1.1
Analogical phase voltage (kV)	−2000
Digital phase voltage (kV)	1000
Scanning mode	Peak-jumping
Dwell time (ms)	100
Number of points/peak	9
Number of readings/replicate	50
Number of replicates	3
Reaction gas, CH_4 (mL min^{-1})	0.4
Distance from rotary valve to nebulizer (cm)	52.3
Isotopes	^{195}Pt, ^{106}Pd, ^{193}Ir

constituents [10]. Therefore, coupling of a separation/preconcentration procedure and elimination of interfering species prior to detection is necessary [11]. Among different separation techniques solid phase extraction (SPE) based on adsorption, ion-exchange or chelating properties of solid sorbents has been demonstrated to be most effective. Different sorbents such as Amberlite XAD-16 [12], Dowex resins [13,14], activated alumina [15], modified silica gel [16–18], polyaniline (PANI) [19] and various chelating resins such as Metalfix-Chelamine [20], functionalized mesoporous silica (APS–MCM–41) [21], PSTH-Dowex [22,23], have been used for the separation/ pre-concentration of PGMs. On the other hand, spectral interferences in ICP-MS determination have been corrected using mathematical correction equations based on signal ratio measurement [1], but this technique is inefficient during determination of Pd [24].

The aim of this paper is to develop a reliable method for on-line separation, pre-concetration and simultaneous determination of Pt, Pd and Ir from environmental samples by on-line column pre-concentration/ICP-MS using a chelating resin, synthesized, characterized and applied by us [1,5-bis(2-pyridyl)-3-sulphophenyl methylene] thiocarbonohydrazide bonded to aminopropyl-controlled pore glass (PSTH-cpg) [25,26]. The determination of Rh is not attempted in this study because the only isotope available for this element is affected by spectral overlaps. Resano et al. [27] have demonstrated that the use of dynamic reaction cell (DRC) pressurized with NH_3 significantly reduced interferences on Rh but this approach is not available in our ICP-MS instrument.

On the other hand, in developing a preconcentration and matrix separation on solid sorbents procedure, one needs to adjust some variables in order to establish optimum conditions for the analysis. This can be very time-consuming if a conventional univariate optimization is undertaken manually and, where interactions exist between the variables, one is unlikely to find the true optimum [28]. A fruitful way to conduct experimental designs and optimization is according to surface—response methodology (SRM), which includes a group of mathematical-statistical techniques that were designed to optimize the analytical response by producing a model in which a response function corresponds to several variables called factors [29]. In this paper, factorial design was applied for optimization of some experimental variables.

The accuracy of the proposed method was checked with certified reference materials. Values obtained were in accordance with those reported for the certified materials. The method was applied to the determination of Pt, Pd, and Ir in marine sediment and water samples from different origins (sea and river).

2. Experimental

2.1. Reagents

All reagents used were of the highest available purity. All plastic and glassware were cleaned with hot concentrated nitric acid and stored soaked in 10% v/v nitric acid, they were rinsed several times with water immediately before use. Doubly de-ionized water (DDW) (18 MΩ cm^{-1}) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout. The column was packed with PSTH-cpg according to a previous paper [25]. Multielement standard solutions of Pt(IV), Pd(II), and Ir(III) for calibration were prepared daily by two stage dilution of 1000 mg L^{-1} stock solutions (Merck, Darmstadt, Germany). A pH 3.2 buffer solution of 0.2 M was prepared using acetic acid (Fluka) and sodium acetate (Fluka). A 0.03% (m/v) thiourea (Merck) solution in 3.2% (v/v) nitric acid was used as eluent.

2.2. Instrumentation

A Perkin-Elmer ELAN DRC-e inductively coupled plasma mass spectrometer (Perkin-Elmer SCIEX Instruments, Concord, Canada) equipped with an autosampler AS-91 was used throughout. The instrument, with standard nickel sampler and skimmer cones, was optimized daily and operated as recommended by the manufacturer. The nebulizer gas flow rate was adjusted so that the CeO^+/Ce^+ ratio and Ba^{++}/Ba^+ were less than 3%. The optimum operation conditions were summarized in Table 1. A Perkin-Elmer FIAS-400 AS system, which consists of two peristaltic pumps and a five way rotary valve, was used as the flow injection accessory and controlled by the ELAN DRC-e software. The FIAS-400 AS system was connected directly to the ELAN DRC-e by means of a 52.3 cm long narrow-bore Teflon tubing (0.8 mm i.d.), the least possible distance to avoid sample dispersion. The mini-column packed with the chelating resin was placed in the sample loop of the rotary valve. This mini-column was a glass tube (3 cm × 3 mm i.d.), the resin was packed to a height of 1.2 cm, at both ends of the mini-column polyethylene frits (Omnifit, Cambridge, UK) were fixed to prevent material losses.The data acquisition for the on-line column pre-concentration was obtained using peak height maximum with 100 ms dwell time and 50 readings for the measurement. Methane was used as a reaction gas in order to reduce the noise, which is fundamental to the improvement of detection limits.

An Anton Paar (Graz, Austria) Multiwave 3000, microwave oven equipped with a XF-rotor and XF-100 digestion vessels was used for the digestion of the solid samples.

2.3. Sample preparation

The certified reference material (CRM) analyzed to determine the accuracy of the proposed procedure was: National Institute of Standards and Technology (NIST), NIST-2557 autocatalyst. The samples was first dried in accordance with the instructions of the analysis certificate, after which an accurately weighed amount of 0.250 g was subjected to microwave digestion as follows: 1.5 mL of concentrated HNO_3, 4.5 mL of concentrated HCl and 2 mL of concentrated HF were added to the weighed amount of sample into the digestion vessel. Four vessels were put into the microwave oven at 600 W of power with 10 min ramping time and 15 min heating time. At the end of the digestion program the vessels were allowed to cool for 20 min before removing them from the microwave unit. After which, samples were evaporated to small volume and the pH of the solutions was adjusted to 3.2 with NaOH and buffer solutions and, finally, the samples were diluted to 250 mL with de-ionized water in a calibrated flask.

Blanks were prepared using the same procedure without the addition of sample.

The sediment samples were collected by using a dredge and were placed in plastic sample bags for transportation to the laboratory. The samples were dried at 105 °C for 24 h in an electric oven, homogenized, sieved into 2 mm, 2 mm–75 μm and 75 μm fractions and stored at room temperature in sealed secure polypropylene containers to avoid contamination. All analysis was performed to the silt (<75 μm) fraction which was grounded to highly homogeneous fine-powder with an agate polytetrafluoroethylene ball mill. The procedure for sample preparation was the same that for the certified reference material aforementioned.

Natural waters were collected in polypropylene bottles (previous cleaned by soaking for 24 h in 10% v/v nitric acid and finally rinsed thoroughly with ultrapure water before use) from coastal surface seawater of Malaga Bay and from surface water of Guadalhorce River (Málaga), samples were immediately filtered by using 0.45 μm pore size cellulose nitrate filters from Millipore. After that, the samples were acidified to 0.1% v/v by the addition of concentrated HNO_3 and stored in a refrigerator at 4 °C as recommended by Method 3010 B from the Environmental Protection Agency (USA), for less than 3 day until analysis.

For the analysis of these samples, aliquots of them (previously neutralised with diluted NaOH) were placed in volumetric flasks of 25 mL, then 2.5 mL of acetate-acetic acid buffer of pH 3.2 and de-ionized water were added up to the mark. Samples were analyzed, in triplicate, immediately after preparation, by introducing them into the manifold depicted in Fig. 1.

2.4. On-line column preconcentration/ICP-MS procedures

Schematic diagrams for sample loading and elution of trace metals from the column by the on-line column preconcentration/ICP-MS method are shown in Fig. 1. The operation parameters of this system are presented in Table 2.

Daily, the system, in the load position, was cleaned using 5% v/v nitric acid during two minutes and then washed by MQ water. Following, blank and calibration standard solutions were measured by the on-line column preconcentration/ICP-MS procedure. Then, after washed by MQ water, the sample solutions adjusted at pH 3.2 were measured. The on-line column procedure was as follows: during the 3 min preconcentration step, valve in the “fill” position, a 1.1 mL min^{-1} flow of sample (standard or blank) is pumped (via pump 1) through the minicolumn (located in the loop of the valve) while the peristaltic pump 2 pumped eluent into the nebulizer. The metal ions are adsorbed on the chelating minicolumn and the sample matrix sent to waste. Before the elution step, DDW is pumped through the mini-column for 1 min to remove salt residues from the sample matrix and then the sample pump P1 is stopped. The valve is turned to the elution position and the eluent (0.03% thiourea in 3.2% nitric acid) passes through the minicolumn in a reverse flow relative to the preconcentration step (avoiding the continuous increase in column compactness). Thus, the accumulated metal ions are eluted at an elution rate of 2.1 mL min^{-1} for 2 min and the metal signals were measured. Finally, the valve turns again to fill position for a new sample loading period. This process is repeated three times, number of replicates programmed in the method. Transient signals were measured as peak height by using instrument software.

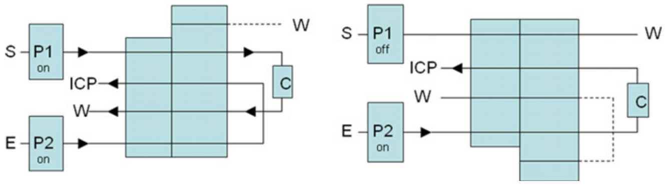

Fig. 1. Schematic diagrams of on-line preconcentration and eluting procedure.

Table 2
Optimum operating conditions for FIAS system.

Step	Solution	Valve position	Flow rate (mL min^{-1})	Time (s)	Direction
Prefill	MQ water	1	1.1	45	Waste
	0.03% Thiourea in 3.2% HNO_3	1	2.1	45	ICP-MS
Sample loading period	Sample	1	1.1	180	Waste
	0.03% Thiourea in 3.2% HNO_3	1	2.1	180	ICP-MS
Wash period	MQ water	1	1.8	60	Waste
Elution (Pump 1 off)	0.03% Thiourea in 3.2% HNO_3	2	2.1	120	ICP-MS

2.5. Optimization strategy

A rotable uniform central composite design (CCD) [30] was used to study the empirical relationship between three controlled factors. The selected factors and their corresponding ranges were determined after preliminary experiments. These factors were pH, thiourea concentration and HNO_3 concentration. The lower and upper values given to each factor were 1.0 and 5.0 for pH, 0.01% and 0.03% for thiourea concentration and 1.0 and 3.2% for HNO_3 concentration. The CCD used includes a 2^3 factorial design (8 experiments), a 2×3 start design (6 experiments) and 3 center points. The resulting 17 experiments were randomly performed. The data were processed by using the Statgraphics Centurion software (version 16.1.11 for Windows). For CCD, the significance of the effects was checked by analysis of the variance (ANOVA) and using p-value significance levels.

3. Results and discussion

3.1. Optimization of the experimental variables

To optimize the system, most efforts were focused on the conditions for sample loading and simultaneous analytes elution from the column, as well as the flow system which was coupled on-line with the pre-concentration and separation unit in order to obtain highly sensitive, accurate and reproducible results. Also, the wash step of the mini-column, after the sample loading, was specially studied. For measurements to be useful, it was considered that a relative standard deviation (R.S.D.) of about 8% was acceptable. The best analyte-to-blank signal ratios were chosen as the optimization criterion. All analyses were performed in triplicate.

3.1.1. Solid support selection

Establishment of experimental parameters for optimization was initiated by finding the appropriate sorbent material for the analytes aforementioned. A chelating resin studied by us is PSTH-cpg, this chelating resin has good chemical properties as chelating reagent, is stable over a wide pH range (0–13), besides being stable for a very long time. In addition, this chelating resin has no affinity for sodium, potassium, calcium or magnesium cations [25]. The organic ligand PSTH adsorbed on an anion-exchange resin (Dowex 1X8-200) has been used, for preconcentration and determination of trace amounts of platinum [22] and palladium [23] with good results. The principal advantage of PSTH-cpg with respect to PSTH-Dowex resin is its very good stability and resistance because chemisorption of chelating molecules on the surface of solid supports provides mechanical stability, immobility and insolubility. Thus, the PSTH-cpg minicolumn has a practically unlimited lifetime without the demand of regeneration. Also, it presents some advantages compared with other ion-exchange resins; e.g. high amounts of concentrate mineral acids are not necessary for the elution of the PGMs on the column or large columns are not necessary for a good retention of the PGMs on the column as happens with some cation-exchange resins. On the other hand, the geometry of the glass allows high sample flow rates with low back-pressure. In addition, PSTH-cpg is a low cost compared with other chelating sorbents and the material can be stored and applied conveniently. For these reasons PSTH was chosen as chelating resin for this study to design a system for separation and preconcentration of Pt, Pd and Ir in the same injected sample.

3.1.2. Selection of eluent

To minimize the time needed for quantitative elution and to facilitate eluate delivery, dispersion during elution must be reduced, while a highly efficient eluent should be used. A mixture of thiourea and nitric acid was chosen as the eluent owing to its effective elution of the three adsorbed metals, its easy direct delivery through the peristaltic pump tubing and its low toxicity.

3.1.3. Effect of pH and eluent concentration on the collection and elution of Pt, Pd, Ir

The optimization of the pH, concentrations of thiourea and nitric acid were carried out by applying the experimental design methodology. A CCD involving 17 runs was performed in order to obtain the optimum conditions with the three continuous variables found to be potentially significant for this method. Three dimensional representations keeping one of the variables at the optimum value are presented in Fig. 2. The data indicate that interactions usually occur between principal factors. This means that the response surfaces in the factorial space are curved in the domain of the experimental design. The results showed that the optimum working conditions for the simultaneous determination of Pt, Pd and Ir were: sample pH of 3.2, thiourea concentration of 0.03% and HNO_3 concentration of 3.2%.

3.1.4. Selection of FI variables

The univariate method was used to determine the best experimental conditions. The sample flow rate is a very important operational parameter for the preconcentration efficiency and it determines the sample volume to be used. In general, for on-line system the sample flow rate is limited by its pressure and/or sorption efficiency. The effect of the sample flow rate for the ICP-MS signals was investigated in the range 0.8–1.8 mL min^{-1}, using a constant sample volume of 1.6 mL. In general, the ICP-MS intensities of metals increased as the sample flow rate decreased. These variations are probably due to kinetic factors, with a greater uptake being observed at lower flow rates. However, since the analysis time increases when the sample flow rate is slow, a 1.1 mL min^{-1} of sample flow rate was selected.

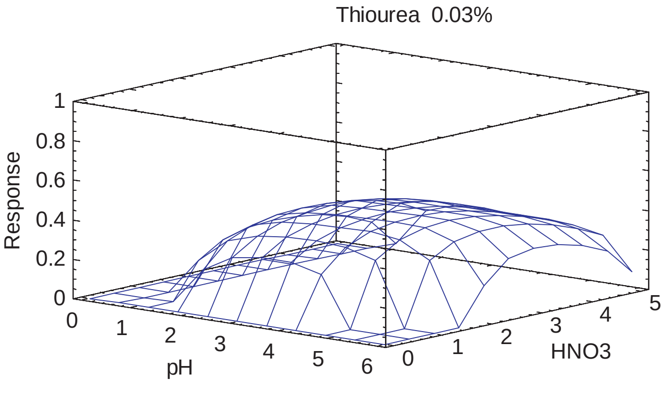

Fig. 2. Estimated response surface.

For quantitative desorption of the retained analytes in a small eluent volume, which is needed for a high enrichment factor, a low elution flow rate should be used, providing sufficient time for equilibrium between the solid-phase and the eluent. The effect of the elution flow rate was studied between 0.8–3.0 mL min^{-1}. The best analyte-to-blank signal ratios were obtained with an elution flow rate of 2.1 mL min^{-1}. An increased rate of eluent flow decreased the width of the elution peak and reduced the analysis time. However an increased rate of eluent flow also decreased the nebulization efficiency, thereby decreased the ion signal significantly.

With all experimental variables optimized, the effect of the sample loading time on the analytical signal of a 5.0 $\mu g\ L^{-1}$ standard of three analytes was studied at a sample flow rate of 1.1 mL min^{-1}. For all analytes the signal increased linearly at least up to a 9 min preconcentration time. The sensitivity was increased by increasing the sample loading time; however, when sample loading time is longer results in lower sampling frequency, in addition, it is less cost-effective since it will require the use of larger quantities of chemicals. Taking this into consideration, a pre-cocentration time of 3 min was selected to achieve a good sensitivity and sampling frequency. A longer loading time can be employed for samples with low concentrations of the analytes.

3.1.5. Effect of matrix elements

ICP-MS methods for the determination of PGMs very often appears to be difficult, because of the complexity of environment samples matrices, which give rise to interferences [3]. The consequence of signal overlap is a positive bias on the analyte concentration reported. As indicated in the literature, many of these problems can be reduced or eliminated by using a dynamic reaction-cell (DRC) [31].The method developed here uses a DRC pressurized with methane because in this mode the blank values were significantly lower than in the standard mode and the detection limits (LODs) were significantly better. The flow rate of the reaction gas (methane) was optimized according to manufacturer instructions. The optimized flow rate of methane was 0.4 mL min^{-1}.

Despite the use of the reaction gas, the mini-column must be washed after the sample loading in order to removal of matrix residues from the sample that could be present in the dead volume of the mini-column and possibly pose a potential source of error. For removing the matrix elements the column was washed by DDW or buffer solution (pH 3.2) at different concentrations, at a flow rate between 0.8 and 2.1 mL min^{-1} and with washing time between 1 and 2 min. In general, the best results for the three analytes were obtained by 1 min washing time with DDW using flow rate of 1.8 mL min^{-1}.

3.1.6. Performance of the method

Under the optimum conditions described above, the performance data of the on-line FI–ICP-MS system for the simultaneous pre-concentration and determination of Pt, Pd and Ir were

Table 3
Analytical performance.

Figure of merits characteristic	Pt	Pd	Ir
Sampling frequency (sample h^{-1})	10	10	10
Enrichment factor	18	2.3	43
Detection limit (ng L^{-1})	78.5	55.5	0.1
Precision (%) (RSD, $n=10$)	3.0	3.0	3.0
Calibration functions*	$y=2910x+219$	$y=11108x+3036$	$y=5019x+228$
Correlation coefficient	$R=0.999$	$R=0.989$	$R=0.999$

* *y*, signal (cps); *X* concentration (ng L^{-1})

Table 4
Comparison of the analytical performance of the present method with literature data.

Sorbent	Analyte	Technique	LOD (ng mL^{-1})	Enrichment factor	Sample volume (mL)	Eluent	Precission (%)	Robustness of the resin	Sampling frequency (h^{-1})	Reference
PANI	Pd	ICP-MS	0.0019	125	250	0.03% Thiourea in 3% HCl	<3	10 times	–	[21]
Dowex AG50-X8	Rh, Pd, Pt, Ir	ICP-MS	–	1–7.8	–	0.5 M HCl	1.5–12.5	The resin was discarded after each sample	–	[15]
Dowex 1-X8	Au, Rh, Ru, Pd, Pt, Ir	ICP-MS	0.06–0.17	–	–	0.3 M Thiourea in 0.1 M HCl/HCl 12 M	–	The resin was discarded after each sample	–	[32]
Aminopropyl-silica gel	Pt	ICP-MS	0.001	50	250	1 M Thiourea in HCl (pH=0.5)	5	–	33	[33]
PSTH-cpg	Pd, Pt, Ir	ICP-MS	0.001–0.055	2.4–43	3.3	0.03% Thiourea in 3.2% HNO_3	3	At least one year	10	This work

obtained and are presented in Table 3. A linear calibration graph was obtained at least until 600 ng L^{-1} Pt, Pd and Ir. The enrichment factors were calculated as the ratio of the slopes of the linear sections of the calibration graphs with and without preconcentration. The detection limits (LODs) were calculated as the concentration of analytes giving signals equivalents to three times the standard deviation of the blank plus the net blank intensity. The precisions were evaluated as the relative standard deviation obtained after analyzing six series of six replicates of a standard containing ten times more concentration than the detection limit of the each analytes.

Although is difficult to compare the figures of merit for the developed method directly with results from others workers, because of different experimental conditions such as column dimensions, sample flow rate, etc, some estimates can be made. For comparison, the analytical performance data of some similar methods reported in the literature were listed in Table 4. As can be seen in this Table, the robustness of the PSTH-cpg resin is better to those reported for other sorbents. On the other hand, the higher enrichment factor reported in some references was obtained using a large volume of sample solution.

3.1.7. Analytical application

The proposed procedure was validated through the determination of the metals in a certified reference material NIST-2557 autocatalyst. The results, as the average of four separate determinations, are shown in Table 5. These results are in agreement with the certified values. On the other hand, in order to test the application of the method to the simultaneous determination of Pt, Pd and Ir in natural environmental samples, known amounts of three analytes were added to marine sediment, seawater and river water samples. The results, shown in Table 4, indicated good recovery in all instances, values from 93 to 107% were obtained. These results indicate that the present method is reliable enough to apply to the multielement determination of trace elements in these samples.

4. Conclusions

Our experiments demonstrated that Pt, Pd and Ir can be quantitatively adsorbed onto PSTH-cpg resin and eluted using a one-stage procedure. The proposed flow injection system enables effective on-line Pt, Pd and Ir preconcentration and final determination improving the selectivity of the ICP-MS and reducing analysis time, sample and reagents consumption and sample contamination. Sample volumes of 3.3 mL resulted in enrichment factors of 18, 2.3 and 43 for Pt, Pd and Ir, respectively, and permitted the determination of ng L^{-1} levels of three analytes with LOD of 78.5 ng L^{-1} for Pt, 55.5 ng L^{-1} for Pd and 0.1 ng L^{-1} for Ir. This system is sufficiently fast, allowing a throughput of 10 samples h^{-1}, as to be useful for routine sample analysis. On the other hand, the PSTH-cpg mini-column presents some advantages compared with other ion-exchange resins: it has a practically unlimited lifetime without the demand of regeneration, high amounts of concentrate mineral acids are not necessary for the elution of the PGMs on the column or large columns are not necessary for a good retention of the PGMs on the column as happens with some cation-exchange resins. On the other hand, the geometry of the glass allows high sample flow rates with low back-pressure. In addition, PSTH-cpg is a low cost sorbent compared with other chelating sorbents and the material can be stored and applied conveniently.

Table 5
Analytical applications. The concentrations were in μg g^{-1} for solid samples and μg L^{-1} for water samples.

	Element	Certified value	Added amount	Found[a]	Recovery (%)
NIST-2557 autocatalyst	Pt	1131 ± 11	–	1105 ± 30	98
	–	–	500	1605 ± 110	99
	–	–	1500	2710 ± 110	103
	Pd	233.2 ± 1.9	–	250 ± 40	107
	–	–	2000	2285 ± 15	102
	–	–	3000	3205 ± 55	99
	Ir	–	–	55 ± 5	–
			500	540 ± 15	97
			1500	1535 ± 135	99
Marine sediment	Pt	–	–	–	–
			0.25	0.244 ± 0.009	98
			0.50	0.506 ± 0.009	101
	Pd	–	–	–	–
			0.25	0.253 ± 0.003	101
			0.50	0.506 ± 0.008	101
	Ir	–	–	–	–
			0.25	0.26 ± 0.01	104
			0.50	0.500 ± 0.001	100
Sea water	Pt	–	–	–	–
			3	2.8 ± 0.1	93
			5	5.10 ± 0.01	102
	Pd	–	–	–	–
			3	2.8 ± 0.2	93
			5	5.2 ± 0.1	104
	Ir	–	–	–	–
			3	3.0 ± 0.2	98
			5	5.1 ± 0.1	101
River water	Pt	–	–	–	–
			2	1.9 ± 0.2	95
			4	4.05 ± 0.07	101
	Pd	–	–	–	–
			2	1.9 ± 0.2	95
			4	3.95 ± 0.07	99
	Ir	–	–	–	–
			2	1.9 ± 0.1	95
			4	4.2 ± 0.2	105

[a] Mean ± SD for three replicate measurements of four individual samples.

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