

Preconcentration of Trace Amounts of Platinum in Environmental Samples on Different Sorbents: A comparative study

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Abstract

Since the introduction of the catalytic cleaning of vehicle exhaust gases, platinum is discussed as environmentally relevant element. Increasing Pt concentrations have been reported from a number of countries. The determination of platinum in biological and environmental materials at the "natural" level was made possible by the development of extremely sensitive analytical methods. Two different sorbents for platinum preconcentration in catalyst, water, soil and vegetation were investigated: silica gel functionalized with 1,5-bis(di-2-pyridyl)methylene thiocarbonylhydrazide (DPTH-gel) and [1,5-Bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonylhydrazide (PSTH) immobilised on an anion-exchange resin (Dowex 1x 8-200)]. The sorbents were tested in a microcolumn, placed in the autosampler arm, at the flow rate 2.4 ml min⁻¹. Elution was performed with 2 M nitric acid. Satisfactory results were obtained for two sorbents.

Keywords Platinum; Preconcentration; Microcolumn; Flow injection; Electrothermal atomic absorption spectrometry

1. Introduction

Platinum was included into the investigations since the widespread introduction of the catalytic cleaning of the exhaust gases from motor cars. The determination of trace levels of platinum requires sensitive analytical methods where a separation and preconcentration step is often applied to remove matrix interferences and preconcentrate the analyte to a level that can be reliably determined.

In recent years the development of analytical methods for the determination of platinum has increased. A few reviews on platinum determination in environmental and biological material have been published [1-5].

A number of sorbents and resins have been applied to the preconcentration of platinum and other precious metals. Pt and Pd in natural water [6] have been concentrated on charcoal. Pt in natural water was determined by FAAS after preconcentration on a microcolumn of alumina [7] with flow injection and on-line operation. A procedure was developed for the determination by ICP-MS of Pt, Pd, Ru and Au using an anion-exchange resin for samples containing concentrations of precious metals than 1 µg g⁻¹ [8]. Anion exchange resins were applied also for preconcentration of Pt and separation of matrix elements for the determination of Pt in airborne particulate matter by ICP-MS [9,10]. Other work has involved applications of XAD-4 resin for the retention of Pt, Pd and Rh as chelates [11] and Sraffion NMRR resin to concentrate platinum group elements (PGE) and Au [12].

For many years, atomic absorption spectrometry (AAS), both flame (FAAS) and electrothermal (GFAAS) have been popular instrumental technique for determinations of elements. Work involving FAAS include the determination of Au in geological materials [13-15], and of Pt in natural water [7]. GFAAS has been used for determinations of precious metals in reference materials (RMs) [16-20], Pt, Pd and Au in vegetation [21] and Pt in environmental samples [22] and water [7]. Table 1 contain information about these procedures.

In this work, the usefulness of two different sorbents for platinum preconcentration was studied and compared. An on-line preconcentration procedure was realized by the flow injection technique combined with GFAAS detection.

Table 1 Applications of atomic absorption spectrometry

Sample	Elements	Procedure	Ref.
RMs	Au	HCl-Br ₂ ; Te coprecipitation	13
RMs, rocks	Au	Aqua regia-Br ₂ ; adsorption	14
Natural water	Pt	Microcolumn of alumina	7
RMs	Pt, Pd, Rh, Ir, Ru	Collector: NiS; PGE dissolved	16
RMs (chromitites)	Pt, Pd, Rh, Ir, Ru	Collector: NiS; Flux contained 1:1 mixture of Na and Li tetraborates; PGE dissolved	17
RMs	Pt, Pd	Aqua regia-HF; solvent extraction	18
RMs	PGE, Au	Aqua regia-HF; ion exchange	19
RMs	PGE, Au	Aqua regia-HF; Te coprecipitation	20
Biotic, environmental samples	Pt	Acid digestion, PTFE bomb; electrodeposition	22

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Zeeman/4100 ZL atomic absorption spectrometer equipped with an AS-70 furnace autosampler was used throughout. Pyrolytic graphite coated tubes with pyrolytic graphite platforms were used in all experiments. The light source was a platinum hollow cathode lamp operated at 15 mA; the selected wavelength was 265.9 nm with a spectral slit width of 0.7 nm. The peak area was the signal measurement.

The graphite furnace temperature program for the determination of platinum is shown in Table 2.

The microcolumn containing the DPTH-gel or PSTH-Dowex was a glass tube (3 cm x 3 mm id) packed to a height of 0.5 cm; at both ends of the microcolumn, polyethylene frits were fixed to

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Table 2 Graphite furnace temperature programme ($V_i=40 \mu\text{l}$)

Step	T/°C	Ramp time/s	Hold time/s	Argon flow rate/ml min ⁻¹
1	110	1	40	250
2	130	4	30	250
3	1600	5	20	250
4	2200	0	5	0
5	2400	1	2	250

prevent material loss. On the end of this column was placed a piece of sample capillary of the sampler arm, in imitation of the sample tip of the sampler arm. Thus the sample tip of the sampler arm was replaced with this microcolumn, permitting normal working of the sampler.

A peristaltic pump, P (Gilson Minipuls 3), fitted with a vinyl pump tube (1.65 mm id), was used for loading of the sample. A Rheodyne Type 50 six-port rotary valve was used as a switching valve. Transport lines were made using 0.8 mm id Teflon tubing. The peristaltic pump and the selection valve were readily controlled electronically via two switches on the autosampler that were actuated when the autosampler arm was down. The process was thus fully automated without altering the software of the AA spectrometer. For sample digestion, a microwave oven, Microdigest 301 controlled by Prolabo TX-32, was used. All glassware used was washed with 10 % nitric acid for 24 h and rinsed with de-ionised water immediately before use.

2.2. Reagents

Analytical- reagent grade chemicals were used throughout. PSTH-Dowex and DPTH-gel were synthesised as described elsewhere [23,24]. A standard $1000 \mu\text{g ml}^{-1}$ Pt(IV) solution (CertiPUR, Merck) was used. A pH 5.0 buffer was prepared by mixing 14.8 ml of 0.2 M acetic acid with 35.2 ml sodium acetate and diluting to 100 ml with de-ionised water and a pH 9.4 buffer was prepared by mixing 25 ml of 0.2 M glycine with 8.4 ml of 0.2 M sodium hydroxide and diluting to 100 ml with de-ionised water. HNO_3 (Merck) 2 M was used as eluent.

2.3. Sample preparation

The certified reference material (CRM) analysed to determine the accuracy of the proposed procedures was National Institute of Standard and Technology (NIST), Standard Reference Material (SRM) 2557 catalyst. The sample was first prepared in accordance with the instruction of the analysis certificate, after which an accurately weighed amount of 0.1 g was subjected to microwave digestion. The working condition of the microwave oven is listed in Table 3. After digestion, the excess acid is removed by addition of NaOH solution and, finally, the sample was diluted to 100 ml with de-ionised water in a calibrated flask.

In view of the application of the method to the determination of platinum in other samples, the ability to recover platinum from samples of vegetation and soil spiked with platinum were investigated. For this purpose, standard solutions containing platinum were added to 0.2-0.5 g of bignonia leaves, pinus leaves and soil, and the resulting material was mineralized by microwave digestion as are listed in Table 3. As can be seen from the table, catalyst and soil were mineralized in two steps with addition of HCl and HNO_3 as reagents in the first step while for bignonia or pinus leaves addition of reagents (step 1,2,3: HNO_3 ; step 4: H_2O_2) were needed in the four steps for complete digestion.

River and sea waters were collected in polypropylene bottles previously cleaned by soaking in 0.1 M hydrochloric acid. Samples were filtered by using a membrane of $0.45 \mu\text{m}$ pore size,

acidified to 0.1 % (v/v) with concentrated HNO_3 and stored frozen until analysis. The composition of the synthetic sea water was (in g l^{-1}): 27.9 of NaCl, 1.4 of KCl, 2.8 of MgCl_2 , 0.5 of NaBr and 2.0 of MgSO_4 , according to the specifications of R.C. Weast [25].

Table 3 Working conditions for microwave oven

Step		1	2	3	4
Reagent	A*	HCl	-	-	-
	B*	HNO_3	HNO_3	HNO_3	H_2O_2
	C*	HCl	-	-	-
		HNO_3			
Volume (ml)	A	15	-	-	-
	B	10	10	10	5
	C	7.5	-	-	-
Power (%)	A	50	30	-	-
	B	15	30	30	30
	C	15	-	-	-
Time (min)	A	5	10	-	-
	B	10	22	10	5
	C	10	-	-	-

* A: Catalyst, SRM 2557; B: Bignonia or pinus leaves; C: Soil

2.4. Analytical procedure

The FI manifold is shown elsewhere [26]. The sample (standard or blank) solution of optimum pH was passed through the microcolumn at the rate of 2.4 ml min^{-1} for retention of platinum. Platinum was eluted from the microcolumn directly into graphite furnace with $40 \mu\text{l}$ of 2 M HNO_3 , and immediately was determined by GFAAS.

3. Results and discussion

3.1. Optimisation of experimental parameters

Establishment of experimental parameters for optimisation was initiated by finding the appropriate sorbent material for platinum. The chelating resins DPTH-gel and PSTH-dowex were chosen due to its good chemical properties as a general chelating reagents, stables over a wide pH range (0-13) which is used for selecting the ion metal complex, besides being stable for at least one year (all of this study was performed with the same packed microcolumns).

To optimise the system, main efforts were focused on the conditions for sample loading and platinum eluting from the column, as well as the analytical flow system which was coupled on-line with the preconcentration and separation unit in order to obtain highly sensitive, accurate and reproducible results.

Chemical parameters including sample acidity, ionic strength, concentration and volume of eluent, FI variables (loading time, sample flow rate) and ETAAS parameters were optimised according to the procedure described in Experimental.

Since the solution pH affects the extent of complexation which in turn determines the percentage of metal retained by the resin, the preconcentration of platinum from solutions buffered at different pH was studied.

The influence of ionic strength on the preconcentration of platinum was analysed. For this purpose, different concentrations of buffer were used. The results obtained showed that the signal value remains constant for buffer concentration equal or greater than 0.1 M.

It is known that strong acids are effective in dissociating complexes and releasing free metal ions, for these reason different acids were tested. The influence of the volume of eluent used also was studied. The signal increased as the volume

increased up to 35 μl , then remained constant with further increase in the volume of eluent.

The effect of sample loading time on the absorption signal of Pt was tested at a sample flow rate of 2.4 ml min^{-1} . The signal increased almost linearly with the preconcentration time up to several minutes, after which the slope decreased gradually. Sensitivity enhancements gained by increasing the sample loading time, however, the loading time selected in the experiment was 60 s in order to achieve high sampling frequency with a reasonable degree of sensitivity. Loading time may be higher for samples with low concentrations of platinum.

The influence of the sample flow rate was studied using a constant volume of injection of eluent of 40 μl . For this purpose, a fixed amount of platinum were brought to optimum pH and passed through the column at different flow rates. Changes in the flow rate of the sample were studied between 1.6 and 4.7 ml min^{-1} . The optimum conditions obtained are summarised in table 4.

On the other hand, prior to the analysis of real samples it was necessary to optimise the instrumental conditions for the determination of platinum by ETAAS. The complete programme developed as a result of the normal optimisation procedure is as described in Table 2.

3.2 Analytical characteristics of the developed procedures

The characteristic performance data of the FI-GFAAS systems for platinum determination are presented in Table 5. The detection and determination limit was defined as the concentration of analyte giving signals equivalent to three and

ten times, respectively, the standard deviation of the blank plus the net blank intensity. The enrichment factor (EF) was determined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, the concentration efficiency (CE) was defined as the product of the EF and the sampling frequency in number of samples analysed per hour and the consumptive index was calculated as the volume of sample, in millilitres, consumed to achieve a unit EF. These parameters are recommended as criteria for the evaluation of the efficiency and reliability of the design of on-line column preconcentration for flow-injection atomic spectrometric system [27].

Table 4 Optimum experimental parameters

Sorbent	PSTH-Dowex	DPTH-gel
pH range	8.6-10.4	3.6-5.6
Selected pH	9.4	5.0
Ionic strength	0.2 M	0.2 M
Eluent	HNO_3	HNO_3
Eluent volume	40 μl	40 μl
Sample loading time	5 min for 100 ng ml^{-1}	7 min for 2 ng ml^{-1}
Sample flow rate	2.4 ml min^{-1}	2.4 ml min^{-1}

Table 5 Performance of the FI-GFAAS systems for platinum determination under the conditions given on the procedure

Analytical parameters	DPTH-gel		PSTH-Dowex	
	Peak-height	Peak-area	Peak-height	Peak-area
Working concentration range (ng ml^{-1})	0 - 20	0 - 20	0 - 50	0 - 100
Calibration function (C_{Pt} in ng ml^{-1})	$A=0.018C+0.026$	$A=0.029C+0.027$	$A=0.007C+0.037$	$A=0.010+0.041$
Correlation coefficient	0.993	0.997	0.995	0.998
Detection limit (ng ml^{-1})	1.0	0.8	0.5	1.0
Determination limit (ng ml^{-1})	2.3	1.8	3.7	4.0
Precision (% RSD, $n = 11$)	1.0 ($C_{\text{Pt}} = 4 \text{ ng ml}^{-1}$)	1.6 ($C_{\text{Pt}} = 4 \text{ ng ml}^{-1}$)	3.0 ($C_{\text{Pt}} = 10 \text{ ng ml}^{-1}$)	1.6 ($C_{\text{Pt}} = 10 \text{ ng ml}^{-1}$)
Sampling frequency (h^{-1})	29	29	29	29
Enrichment factor	25.7	41.7	7	14
Concentration efficiency(min^{-1})	12.4	20.1	3.4	7
Consumptive index (ml)	0.09	0.06	0.34	0.18

3.3. Effect of foreign ions

The results of including significant levels of possible interferents are presented in Table 6. For this study, different amounts of the ionic species tested were added to a solution of platinum. The starting point was an interferent:platinum ratio of 4000 m/m; if any interference occurred, the ratio was gradually lowered until the interference disappeared. The tolerance limits found show that platinum can be determined in the presence of a variety of ions. The ions that interfere most strongly are those that form complexes with DPTH or PSTH. The interference of diverse ions can be significantly lowered by adding of EDTA to the medium as masking agent to avoid the retention of the interferent into the resins, for example the tolerance level for Co^{2+} can be increased from 10 to 100 m/m.

3.4. Sample Analysis

In order to test the accuracy and applicability of the proposed method for the analysis of real samples, one reference material was analysed. The result, as the average of the four separate determinations, is shown in Table 7. As can be seen, the platinum concentration determined by the proposed methods is in close agreement with the certified value.

In view of the application of the methods to the determination of platinum in other samples, the ability to recover platinum

from samples of water, vegetation and soil spiked with platinum was investigated. For this purpose, standard solutions containing platinum were added to samples and the resulting material was prepared as described under Experimental. Standard additions method was used in all instances and the results were obtained by extrapolation. The results of these analyses are summarised in Table 7, and indicated excellent recoveries in all instances.

4. Conclusions

Sensitive methods frequently in connection with prior preconcentration are required for the determination of platinum in the environment. There are only a few methods enabling their quantitation at extremely low levels, these are adsorptive stripping voltammetry, nuclear activation analysis, GFAAS and ICP-MS. AAS have been used extensively in many laboratories, but detection limits of direct determination, including by GFAAS are thus unsatisfactory. Suitable preconcentration techniques prior to the determination by GFAAS are solvent extraction, sorption and ion exchange.

FI on-line column preconcentration-GFAAS has revolutionised trace element analysis in samples with complicated matrices.

The experiments performed demonstrate that platinum may be quantitatively adsorbed and preconcentrated on two tested

sorbents and eluted with nitric acid. The comparison of different resins has shown that the best enrichment factor of platinum (41.7) was obtained when platinum was eluted with 2 M nitric acid from DPTH-gel microcolumn, while less interference were obtained from PSTH-dowex.

The good recoveries of platinum obtained for platinum determination in environmental samples shows the potential usefulness of the proposed methods for environmental analysis.

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Table 6 Tolerance of foreign ions in the determination of platinum

DPTH-gel	Tolerance ratio m/m	PSTH-Dowex
Ion		Ion
Mg ²⁺ , K ⁺ , Ni ²⁺ , Zn ²⁺ , Cd ²⁺ , Mn ²⁺ , Ba ²⁺ , Br ⁻ , Cl ⁻ , PO ₄ ³⁻ , CO ₃ ⁼ , F ⁻ , EDTA	>4000	Mg ²⁺ , Pb ²⁺ , Ni ²⁺ , Ag ⁺ , Hg ²⁺ , SO ₄ ⁼ , Br ⁻ , ClO ₄ ⁻ , Cl ⁻ , PO ₄ ³⁻ , CO ₃ ⁼ , F ⁻ , EDTA
SO ₄ ⁼ , I ⁻ , SCN ⁻	3000	
	2000	Ca ²⁺ , Mn ²⁺ , Al ³⁺ , Ba ²⁺
C ³⁺	1000	Cr ³⁺
Pb ²⁺ , Cu ²⁺ , Ca ²⁺ , Co ²⁺	500	Cd ²⁺ , SCN ⁻
ClO ₄ ⁻	400	
	250	Cu ²⁺ , Zn ²⁺ , Fe ²⁺ , Fe ³⁺
Fe ³⁺ , Fe ²⁺ , Al ³⁺	200	
	100	Sn ²⁺ , Co ²⁺
Sn ²⁺ , Rh ³⁺ , Zr ⁴⁺	50	
Ce ⁴⁺ , Pd ²⁺	10	Rh ³⁺ , Pd ²⁺

^a With EDTA as masking agent

Table 7 Results for platinum determination in real samples

Sample	DPTH-gel			PSTH-Dowex	
	Certified value (mg kg ⁻¹)	Found value ^a (mg kg ⁻¹)	Recovery (%)	Found value ^a (mg kg ⁻¹)	Recovery (%)
SRM 2557	1131 ± 11	1099 ± 46	97.20	1155 ± 23	102.10
Sample	Added (mg kg ⁻¹)	Found ^a (mg kg ⁻¹)	Recovery (%)	Found ^a (mg kg ⁻¹)	Recovery (%)
Bignonia leaves	125	124 ± 6	99.20	130 ± 7	104.00
Pinus leaves	125	125 ± 2	100.00	127 ± 3	101.60
Soil	50	50 ± 3	100.00	50 ± 2	100.00
Sample	Added (ng ml ⁻¹)	Found ^a (ng ml ⁻¹)	Recovery (%)	Found ^a (ng ml ⁻¹)	Recovery (%)
Tap water	5	5.02 ± 0.16	100.40	5.09 ± 0.11	101.80
	10	10.01 ± 0.40	100.12	10.08 ± 0.07	100.80
River water	5	5.04 ± 0.14	100.80	4.93 ± 0.25	98.60
	10	100.00 ± 0.20	100.00	9.91 ± 0.37	99.10
Sea water	5	4.94 ± 0.33	98.80	5.10 ± 0.23	102.00
	10	9.96 ± 0.15	99.60	10.41 ± 0.41	104.10
Synthetic sea-water	5	5.20 ± 0.27	104.00	5.05 ± 0.09	101.00
	10	9.97 ± 0.25	99.70	9.90 ± 0.29	99.10

^a Mean ± standard deviation, n = 4

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