On-Line Preconcentration of Platinum by Sorption on an Anion-Exchange Resin Loaded with 1,5-Bis(di-2-pyridyl)Methylene Thiocarbohydrazide and Determination by Electrothermal Atomic Absorption Spectrometry

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Abstract

A flow injection on-line sorption preconcentration system for the electrothermal atomic absorption spectrometry determination of platinum has been developed. The method employs on-line preconcentration of platinum on a column packed with silica gel functionalized with 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide (DPTH-gel) placed in the autosampler arm. The modification of the autosampler in the tubing line and circuit allowed either the flow of the sample through the column or the operation of the autosampler in the normal mode, where microlitres of 2 M HNO_3, which acts as the elution agent, pass through the microcolumn eluting Pt(IV), which is directly deposited in the graphite tube as a drop of a precisely defined volume. An enrichment factor of 41.7 and a detection limit of 0.8 ng ml^{-1} along with a sampling frequency of 29 h^{-1} are achieved with 60 s preconcentration time at a sample flow rate of 2.4 ml min^{-1}. The relative standard deviation is 1.6 % for 4 ng ml^{-1} Pt. The method has been applied to the determination of platinum in catalyst, vegetation, soil and waters samples.

Keywords Platinum; electrothermal atomic absorption spectrometry; preconcentration; microcolumn; flow injection

1. Introduction

The increased medical and industrial use of platinum has led to a growing need for its determination in biological and environmental materials:

Platinum is mainly used in automobile exhaust catalytic converters and a catalyst in a wide variety of processes such as nitric acid production and petroleum re-forming. Platinum also finds applications in chemical and glass industries as cladding on account of anticorrosion properties and in electronic industry as material for electrodes, contacts and resistance wires. Another field of application of platinum is the manufacture of jewellery.

Some platinum co-ordination compounds are used in chemotherapy for some types of cancer. Soluble platinum compounds are toxic and chronic industrial exposure to them is responsible for the syndrome called platinosis. Release of platinum from automotive catalytic converters has given rise to environmental and health concerns. Small concentration changes of platinum in the environment and human body must be closely monitored since its environmental and biological impacts are still unclear and have been the object of several studies [1,2]. Therefore, ultra sensitive analytical methods are very desirable, since normal concentrations of the metal in biological samples are below the limit of detection of most analytical techniques [3]. A separation/ preconcentration step is often applied in order to remove matrix interferences and preconcentrate the analyte to a level which can be reliably determined.

Various methods have been developed for platinum separation and preconcentration from environmental and biological matrices, e.g., liquid-liquid extraction [4,5], sorption on XAD-4 resin [6-8], on aminopyridine resin [9], on activated charcoal [10], on activated alumina [11,12], on C_{18}-bonded silica gel [13] or on silica gel funtionalized with aminopropyltriethoxysilane [14]. Most of these methods are off-line and require considerable sample manipulation and long analysis time.

Electrothermal atomic absorption spectrometry (ETAAS) is one of the most sensitive techniques for determination of trace elements. Although ETAAS has very low detection limits for a large number of elements, the direct determination of trace amounts of elements in complicated matrices is usually difficult due to interferences and/or insufficient detection power [15]. Thus, separation of analytes from the matrix is undoubtedly effective in avoiding matrix interferences.

Recently, flow injection (FI) on-line separation and preconcentration techniques have been shown to be efficient in enhancing the selectivity and sensitivity of AAS [16-20].

In the present work, a automatic on-line FI-ETAAS method for the determination of trace amounts of platinum is described. A chelating ion-exchange resin was used for the separation and preconcentration of platinum from different matrices.

2. Experimental

2.1. Reagents

Analytical- reagent grade chemicals were used throughout.

DPTH-gel was synthesised as described elsewhere [21]. A standard 1000 :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. HNO_3 (Merck) 2 M was used as eluent.

2.2. 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

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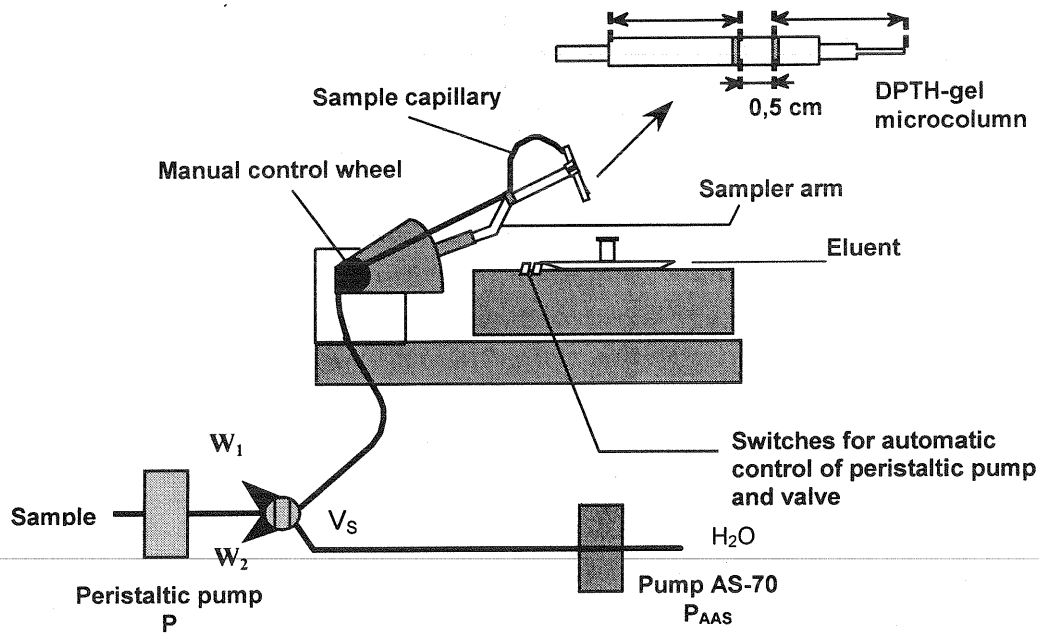

Fig. 1 Schematic diagram of FI-AAS system for the preconcentration, separation and determination of platinum: W_1 and W_2 waste; V_s selection valve. For further detail see text.

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 1.

Table 1 Graphite furnace temperature programme (V_i = 40 µl)

Step	Temperature °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

The microcolumn containing the DPTH-gel 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 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 (Fig. 1). 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. A schematic diagram of the circuit and peripherals is shown in the ESI [22]. For sample digestion, a microwave oven, Microdigest 301 (power released: 200 W) 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.

2.3. Procedure

The FI manifold is shown in Fig. 1. It operated as follows: during the 1 min sample loading period, a 2.4 ml min^{-1} flow of sample (standard or blank) at pH 5.0, buffered with acetic acid-sodium acetate, is pumped (via P) through the microcolumn (located in the sampler arm); the metal ion is adsorbed on the sorbent microcolumn and the sample matrix is sent to waste; then, the switching valve (V_s) is actuated and the pumps of the AS-70 furnace autosampler, P_{AAS}, are connected, permitting the operation of the autosampler in the normal mode; a wash step takes place with de-ionised water and, immediately after, the sampler arm lowers the sample capillary into an autosampler cup (filled with eluent) aspirating 40 µl of 2 M HNO_3; then, the sampler arm swings over to the graphite furnace and the tip of the sampler capillary is inserted into the dosing hole of the graphite tube where the eluted Pt(IV) is deposited as a drop; The sampler arm then returns to its initial position and the cycle of the furnace operation commences (Table 1); while the temperature programme is running, the switching valve is again turned to start a new loading of the sample (standard or blank); thus, when the spectrometer gives the measurement, the microcolumn is ready for a new injection of eluent.

2.4. Sample preparation

The certified reference material (CRM) analysed to determine the accuracy of the proposed procedure 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 2. After digestion, the solution was neutralised with concentrated NaOH 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 prepared by microwave digestion as are listed in Table 2.

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 μm 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 [23].

Table 2 Working conditions for microwave oven

Step		1	2	3	4
Reagent	A[a]	HCl HNO_3	-	-	-
	B[b]	HNO_3	HNO_3	HNO_3	H_2O_2
	C[c]	HCl HNO_3	-	-	-
Volume (ml)	A	15 5	-	-	-
	B	10	10	10	5
	C	7.5 2.5	-	-	-
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

3. Results and discussion

3.1. Optimisation of experimental parameters

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.

In the initial study the stability of the DPTH-gel resin was studied experimentally in acidic, neutral and basic media by observing any physical changes occurring in the material, the results obtained showed that the resin was stable over a wide pH range (0–13).

The preconcentration of platinum from solutions buffered at different pH values was studied. The pH was adjusted from 2.0-3.6 using glycine-HCl buffer, from 4.0-6.5 using acetic acid-sodium acetate buffer and from 7.0-9.2 using boric acid-borax buffer. The optimum pH range was around 3.6-5.6. All subsequent studies were carried out at pH 5.0.

The influence of ionic strength on the preconcentration of platinum was studied. For this purpose, different concentrations of buffer was used. The results obtained showed that the signal value remains constant for buffer concentration equal or greater than 0.1 M. A concentration of 0.2 M of buffer was used for subsequent experiments.

It is known that strong acids are effective in dissociating complexes and releasing free metal ions. In this study a 2 M HNO_3 solution was chosen as eluent.

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. An injection volume of eluent of 40 μl was fixed.

The effect of sample loading time on the absorption signal of 2 ng ml^{-1} Pt was tested at a sample flow rate of 2.4 ml min^{-1}. The signal increased almost linearly up to 7 min preconcentration time, 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 :l. For this purpose, 11.4 ng of platinum were brought to pH 5.0 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}, resulting in an optimum sample flow rate of 2.4 ml min^{-1} with the best signal-to-blank ratio.

Finally, optimum graphite operating conditions were examined. The results obtained are summarised in Table 1.

Table 3 Performance of the FI-ETAAS system for platinum determination under the conditions given in the experimental part

Analytical parameters	Peak-height	Peak-area
Concentration range (ng ml^{-1})	0 - 20	0 - 20
Calibration function (C in ng ml^{-1})	A=0.018C+0.0263	A=0.0292C+0.0277
Correlation coefficient	0.9931	0.9973
Detection limit (ng ml^{-1})	1.0	0.8
Determination limit (ng ml^{-1})	2.3	1.8
Precision (% RSD, n = 11, C = 4 ng ml^{-1})	1.0	1.6
Sampling frequency (h^{-1})	29	29
Enrichment factor	25.7	41.7
Concentration efficiency (min^{-1})	12.4	20.1
Consumptive index (ml)	0.09	0.06

3.2. Performance of the method

The characteristic performance data of the FI-ETAAS system for platinum determination are presented in Table 3. 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 milliliters, consumed to achieve a unit EF [24].

3.3. Effect of foreign ions

The results of including significant levels of possible interferents are presented in Table 4. For this study, different amounts of the ionic species tested were added to a 5 ng ml^{-1} 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 ceased. The tolerance limits found show that platinum can be determined in the presence of a variety of ions. The interference of diverse ions can be significantly lowered by adding of EDTA to the medium.

Table 4 Tolerance of foreign ions in the determination of 5 ng ml^{-1} platinum

Ion or specie	Tolerance ratio m/m
Mg^{2+}, K^{+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Ba^{2+a}, Br^{-},Cl^{-}, PO_4^{3-}, $CO_3^{=}$, F^{-}, EDTA,	>4000
$SO_4^{=}$, I^{-}, SCN^{-}	3000
Cr^{3+a}	1000
Pb^{2+a}, Cu^{2+a}, Ca^{2+a}, Co^{2+a}	500
ClO_4^{-}	400
Fe^{3+a}, Fe^{2+a}, Al^{3+a}	200
Sn^{2+}, Rh^{3+}	50

a. With EDTA as masking agent

Table 5 Results for platinum determination in real samples

Sample	Certified value (mg kg^{-1})	Found value[a] (mg kg^{-1})	Recovery (%)
SRM 2557	1131 ± 11	1099 ± 46	97.20

Sample	Added (mg kg^{-1})	Found[a] (mg $kg.^{-1}$)	Recovery (%)
Bignonia leaves	125	124 ± 6	99.2
Pinus leaves	125	125 ± 2	100.0
Soil	50	50 ± 3	100.0

Sample	Added (ng ml^{-1})	Found[a] (ng ml^{-1})	Recovery (%)
Tap water	5.00	5.02 ± 0.16	100.4
	10.00	10.01 ± 0.40	100.1
River water	5.00	5.04 ± 0.14	100.8
	10.00	100.00 ± 0.20	100.0
Sea water	5.00	4.94 ± 0.33	98.8
	10.00	9.96 ± 0.15	99.6
Synthetic sea-water	5.00	5.20 ± 0.27	104.0
	10.00	9.97 ± 0.25	99.7

a. Mean ± standard deviation, n = 4

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 5. As can be seen, the platinum concentration determined by the proposed method is in close agreement with the certified value.

In view of the application of the method 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 were used in all instances and the results were obtained by extrapolation. The results of these analysis are summarised in Table 5, and indicated excellent recoveries in all instances.

5. Conclusion

Despite its low detection limits, ETAAS is still inadequate when the sample has a complex matrix. In these cases a preliminary preconcentration and/or separation is required. These operations, at one time often the "bottleneck" of the entire procedure, are now completely compatible with an efficient ETAAS sequence. FI-on line column preconcentration-ETAAS has revolutionised trace element analysis in samples with complicated matrices.

The system proposed in this paper has the advantage of being simpler than other FI-ETAAS because the process is fully automated without complicated hardware and software; in fact modification of the software of the spectrometer was not necessary. The use of expensive and sophisticated instruments is also avoided. High speed, ease of use and automation, selectivity and relative freedom from interference make this method suitable for platinum determination in different samples.

The authors thank to the Ministerio de Ciencia y Tecnología for supporting this study (Project BQU2000-0989).

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(Received February 25, 2003)
(Accepted April 24, 2003)