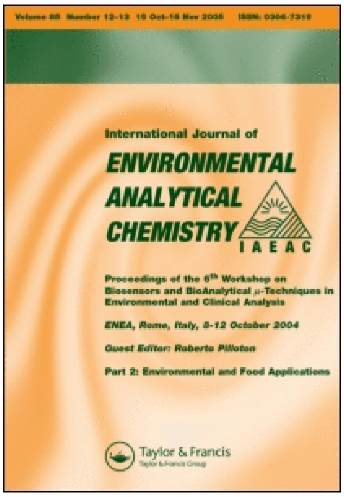

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PRECONCENTRATION OF TRACE AMOUNTS OF PLATINUM IN WATER ON DIFFERENT SORBENTS

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Three different sorbents for platinum preconcentration in water were investigated: alumina, silica gel with bonded aminopropyl groups and Cellex-T. The sorbents were tested in a microcolumn at the flow rate 3 ml/min. Elution was performed with 2.0 mol/l ammonia, 2.0 mol/l hydrochloric acid and 1.2 mol/l thiourea solution, respectively. The optimal enrichment factor was 400 for the alumina column, when the eluent volume was 25 µl. Satisfactory precision was obtained for all sorbents. As the detection technique was used either FAAS or GFAAS, depending on the concentration of platinum in the eluate.

Keywords: Platinum; preconcentration; solid phase extraction

INTRODUCTION

With the introduction of catalytic converters containing platinum, palladium and rhodium the emission of these metals into the environment has increased. The concentration of platinum in dusts emitted from catalysts range from 3 to 40 ng/m3 [1]. It has been found that 30–43% of the total platinum content in airborne dust was in soluble form [2]. Since platinum and other precious metals are deposited along roadways, they can be taken up by plants [1,3] and enter the food chain [1,4]. The studies performed in Australia have shown that 42% of the daily intake of platinum is taken with the diet [4].

In recent years the development of analytical methods for the determination of platinum has increased. A few reviews on platinum determination in environ-

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mental and biological material have been published [3,5–8]. Among the different methods used [1,3,6], adsorptive cathodic stripping voltammetry does not require a separate preconcentration step, although the elimination of matrix interferences is necessary before the measurement [9]. Nuclear methods, both instrumental and radiochemical neutron activation analysis require preliminary separation of platinum from gold [10]. Other techniques as inductively coupled plasma atomic emission spectrometry (ICP-AES) [11], graphite furnace atomic absorption spectrometry (GFAAS) [12,13] and especially inductively coupled plasma mass spectrometry (ICP-MS) have been used in many investigations [14,15].

In order to achieve sufficient sensitivity to determine platinum in natural samples, the preconcentration and separation of the analyte from matrix and interfering elements is necessary. In this respect, several preconcentration procedures have been published in the literature [11–16]. Among them ion-exchange materials are often used. The separation of platinum on ion exchange resins [7,11,16] or sorbent extraction [7] eliminates the solvent extraction and makes possible selective retention of trace amounts of platinum on the column.

The chlorocomplexes of platinum reveal the high affinity for strongly basic anion-exchangers with styrene or acrylic polymers. However, this makes difficult the quantitative elution of platinum and concentrated solutions of mineral acids, sometimes even at high temperature, had been used as eluents [11,17-18]. In some cases even mineralization of the resin was necessary for quantitative recovery of platinum [15]. Preconcentration of platinum using resins containing selective chelating groups, as dithiocarbamates [12] or thiourea derivatives [7], covalently attached to polymeric matrix was also proposed. The collection of platinum on activated alumina was discussed by Cantarero et al. [13]. A flow-injection technique with on-line sample preconcentration on different resins was also developed [11,14,16].

In this work the usefulness of weak-anion exchange sorbents based on different matrices (cellulose, alumina, silica gel) for platinum preconcentration was studied. The use of weakly basic anion exchangers should improve the effectiveness of the platinum elution process. An on-line preconcentration procedure was realized by the flow injection technique combined with flame atomic absorption spectrometry. When lower detection limits were needed an off-line procedure with GFAAS detection was applied.

EXPERIMENTAL

Apparatus and materials

A PU 9100X (Philips Scientific) atomic absorption spectrometer equipped with PU 9390X electrothermal atomizer, FS-90 autosampler and deuterium background correction was used for platinum determination. The platinum hollow cathode lamp (Unicam) was operated at 12 mA current. All measurements were done using standard pyrolytically coated graphite furnaces. The platinum absorbance was measured at 265.6 nm with 0.2 nm spectral bandpass. Optimized temperature conditions for platinum determination by GFAAS are given in Table I.

TABLE I Temperature programme for platinum determination by GFAAS technique

Programme step	*Temperature / °C*	*Hold time / s*	*Ramp time / °C/s*
Drying	110	12	7
	160	10	10
Pyrolysis	1600	8	150
Atomization	2700	2.5	2000[a]
Cleaning	2700	2	2000

a. gas stop

Measurements with flame atomization were carried out on AAS-1 spectrometer (Carl Zeiss, Jena) at 265.6 nm, with 0.2 nm spectral bandwidth, using the above mentioned lamp at 12 mA current. The air-acetylene flame was used.

The on-line sorbent extraction preconcentration system consisted of a peristaltic pump MS-REGLO (Ismatec), rotary valve 5020 RHEODYNE (Cotati CA), PTFE tubing of i.d. 0.8 mm and laboratory-made adsorption columns. The columns (20 mm×3 mm i.d.) were made of PTFE and were packed with alumina, Cellex-T and silica gel with bonded aminopropyl groups. The two end parts of the column were blocked with PTFE membranes.

Reagents and solutions

A standard platinum solution as hexachloroplatinum acid (30%) (POCh, Poland) was used. The standard stock Pt (IV) solution (1 mg/ml) was prepared in 0.1 mol/l hydrochloric acid. Working standard solutions of platinum were prepared daily by appropriate dilution of the stock standard. Hydrochloric acid

(30%) and nitric acid (65%) Ultranal (Cheman) were used. Ammonia (25%), thiourea, sodium chloride, methanol and ethanol were of analytical grade from POCh. The appropriate solutions were prepared by dilution with water. Milli-Q water was used to prepare all solutions.

The following resins were used:

- Cellex-T, highly purified cellulose powder containing quaternary amine exchange groups (TEAE, $(CH_2)_3N^+(CH_3)_3$) (Bio-Rad Laboratories), exchange capacity 0.74 meq/g (producer data),
- alumina, activity grade I, basic form (Sigma),
- silica gel with bonded aminopropyl ($-(CH_2)_3NH_2$) groups (J.T.Baker), exchange capacity 1.6 meq/g (producer data).

Analytical procedure

The 10 ml of sample solution of about pH 2- 2.5 was passed through the microcolumn at the rate of 3 ml/min for retention of platinum. Platinum was eluted from the microcolumn directly into autosampler cups by pumping the appropriate volume of eluent solution at the rate of 0.3 ml/min and immediately was determined by GFAAS. The gas bubble separated the carrier and the eluent solutions. Before the next preconcentration process the column was conditioned with an appropriate solvent (Table II).

When studying the effect of matrix on platinum determination by GFAAS the net absorbance signal of platinum was obtained by subtracting the blank signal from the signal of platinum standard containing the studied matrix compound.

Rigorous precautions were taken to avoid platinum contamination through the procedure. The Milli-Q water, high-purity or cleaned with resin Chelex-100 reagents, all plastic materials and glassware were thoroughly rinsed initially with 2 mol/l nitric acid, next with 1 mol/l hydrochloric acid and finally with water.

RESULTS AND DISCUSSION

Optimization of the adsorption and elution process

The platinum group metals form stable chlorocomplex anions. The effectiveness of platinum preconcentration step was studied on the following sorbents: alumina (in the acidic form), Cellex-T (triethylaminocellulose) and silica gel with bonded aminopropyl groups. Activated alumina can function as a weak cation or a weak anion preconcentrator depending on the pH. Cellex-T is the cellulose exchanger with bonded quaternary amines. This type of resin is characterized by the high rate of the exchange processes and the small change of volume in different media [19]. The silica gel with bonded aminopropyl groups may act as a weak anion exchanger in aqueous medium (pK_a=9.8) or as a polar sorbent in non-polar organic matrix.

The optimization of the method was performed in order to maximise the platinum recovery and to obtain the maximal enrichment factor.

The influence of the sample pH in the range 0.5–10 on the retention of platinum (10 µg) on the column was studied with the FAAS detection. The sample pH was adjusted with hydrochloric acid or sodium hydroxide. It was found that acidity of the solution affects the retention of the metal on different resins (Figure 1). The maximum retention of platinum (98–100%) on the column filled with alumina was achieved at pH range 2–3, while for Cellex-T and modified silica gel resins this pH value of the sample solution may be in the range 2.5–10. Hence, in the further work all platinum standard solutions were adjusted to pH 2.5–3 with hydrochloric acid.

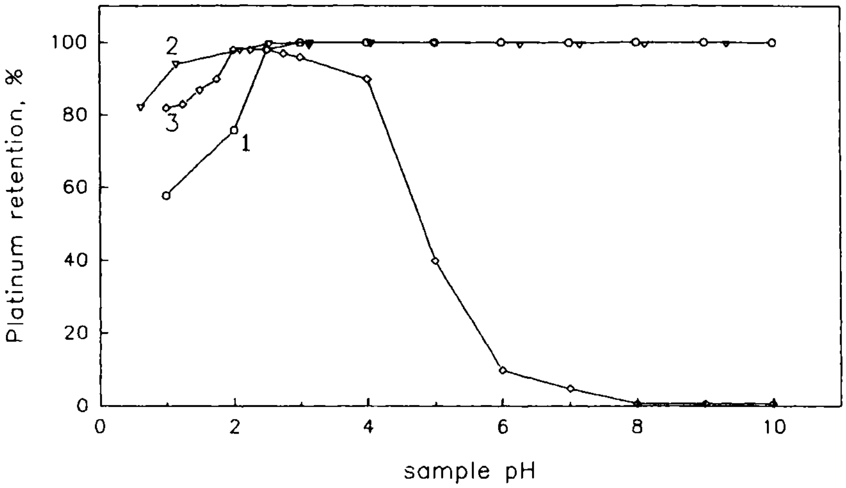

FIGURE 1 The influence of pH on retention efficiency of platinum (in %) on different sorbents. 1- Cellex-T 2- silica gel with bonded NH_2 groups 3- activated alumina

The selection of an effective eluent for each resin was primary performed on the basis of the physico-chemical characteristics of the sorbent and of the chemical properties of the tested compounds. The hexachloroplatinic acid (H_2PtCl_6) at pH 2–3 is partly ionized, promoting the adsorption on the weakly basic anion exchange sorbent. The analyte can be then eluted with an acidic eluent which competes with the analyte for ion-exchange sites, with the solution of higher ionic strength or with compounds which act as stronger complexing reagents than Cl^- ions.

For the column packed with activated alumina the best elution results were achieved for 2 mol/l ammonia solution. The minimal volume of ammonia solution required for completing the elution of Pt(IV) in one step was 25 μl (Figure 2A). The reproducibility of the preconcentration step (n=6) on such microcolumn was 2.2% and the recovery was 103±2.2% (Table II). In this case, a 400-fold preconcentration of platinum solution (for a 10 ml of sample) was obtained. Similar results were obtained by Cantarero et. al. [13] but the precision of measurements for platinum concentration 0.1 μg/ml was 9%.

From the column filled with modified silica gel platinum was eluted with different concentrations of sodium chloride, hydrochloric acid and thiourea solutions. Complete platinum recovery was obtained with 0.9 mol/l sodium chloride, 10% thiourea (pH=1) and 1 mol/l hydrochloric acid. In the case of elution with NaCl an eluent volume as high as 5 ml was required for total platinum recovery. The higher analyte preconcentration factor was found when the thiourea solution was used as eluent. For complete platinum elution from the column in one step 100 μl of the 10% thiourea at pH=1 was needed. The increase of the eluent temperature to 40, 60 and 80°C does not improve the preconcentration factor.

In the case of 1 mol/l hydrochloric acid the 100% recovery was achieved when 200 μl of eluent were used. To achieve an enrichment factor of 400, more concentrated hydrochloric acid (4 mol/l) was required (Figure 2B). However, such acid concentration decreases the sensitivity of platinum detection by GFAAS by approximately 35% and in the further work elution with 2 mol/l HCl (eluent volume 75 μl) was applied. The reproducibility of the preconcentration procedure on that column (n=6) was 1.3% and the platinum recovery 99.8% (Table II).

For the column filled with Cellex-T the usefulness of hydrochloric acid, thiourea, methanol and ethanol as eluents was tested. Ethanol and methanol (with addition of hydrochloric acid) do not remove platinum from the column. To obtain total platinum recovery 200 μl of 2 mol/l hydrochloric acid solution was required. Satisfactory results were obtained by using 1.2 mol/l (8%) thiourea. The minimal eluent volume was 75 μl (Figure 2A) with the enrichment factor of 133. The reproducibility and recovery results are given in Table II.

The study of the flow rate on sample retention and elution showed that relatively high flow rates up to 3 ml/min may be used without decreasing of retention efficiency, while lower flow rates (0.3 ml/min) must be used for complete elution. This is due to ion exchange interactions occuring at a slower rate than

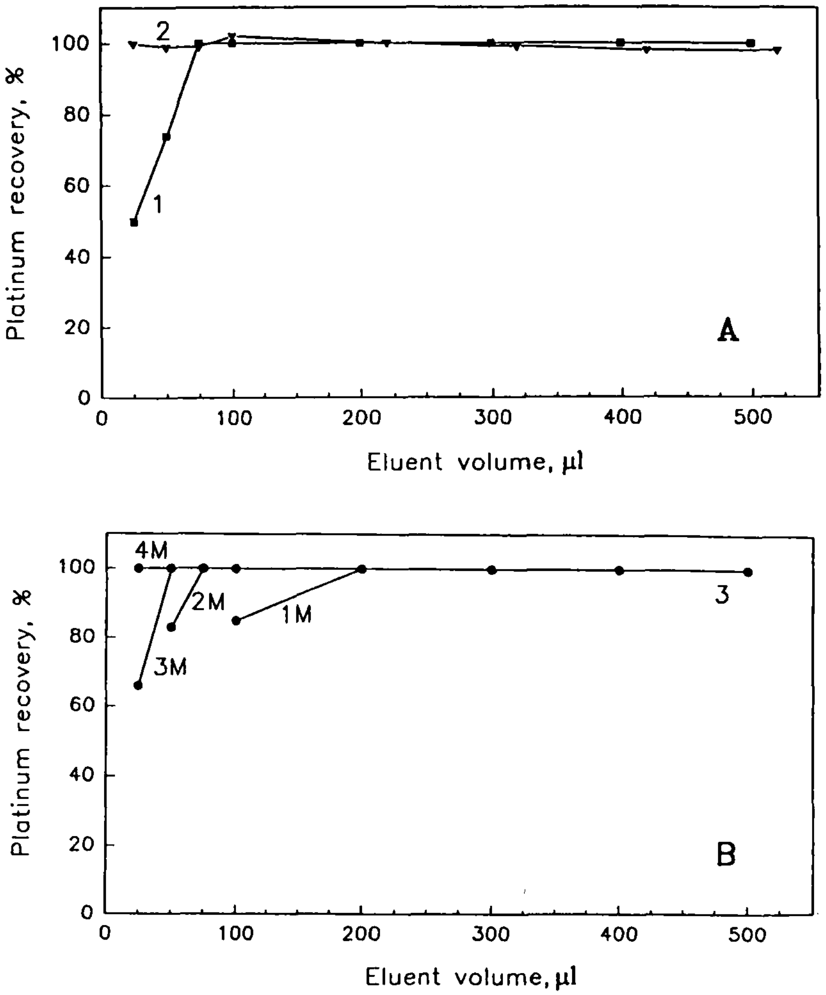

FIGURE 2 The influence of eluent volume and concentration on efficiency of platinum elution from different sorbents A: 1- 1.2 mol/l thiourea (Cellex-T) 2- 2.0 mol/l NH_3 (activated alumina) B: 3- different concentration of HCl (silica gel with bonded NH_2 groups)

polar or non polar interactions. Hence, these flow rates were used in further work.

The breakthrough capacity of columns filled with alumina, Cellex-T and silica gel with bonded aminopropyl groups are, 11.2, 39.0 and 1.6 mg Pt/g sorbent, respectively. Cellex-T resin is characterized by the highest capacity, what is useful in the case of analysis of natural samples.

TABLE II The characteristic of platinum (IV) preconcentration procedure on different sorbents

Parameter	*Sorbent*		
	Al_2O_3	*Cellex-T*	*-NH_2 (silica gel)*
Mass of sorbent	25 mg	10 mg	25 mg
Column conditioning	5 ml of 0.01 mol/l HNO_3	5 ml of water	5 ml of methanol next MQ water
Sample pH	2.5 – 3.0	> 2.5	>2.5
Eluent concentration	2.0 mol/l NH_3	1.2 mol/l thiourea	2.0 mol/l HCl
Eluent volume	25 µl	75µl	75 µl
Enrichment factor (10 ml of the sample)	400	133	133
Breakthrough capacity	11.2 mg Pt/g	39.0 mg Pt/g	1.6 mg Pt/g
Precision (as RSD in %)[a]	2.4	1.0	1.3
Recovery (in %)[a]	103.0 ± 2.2	98.6 ± 1.0	99.8 ± 1.3
Detection limit[b] (GFAAS technique)	15 pg/ml	12 pg/ml	26 pg/ml

a. For 0.29 µg/ml Pt with on-line FAAS detection
b. Recalculated for the solution after preconcentration

Optimization of the determination procedure

For the determination of platinum atomic absorption spectrometry with electrothermal atomization was used and the measurement conditions were optimized. The influence of different eluents on the analytical signal of platinum was investigated and the significant effect was observed in the ammonia and hydrochloric acid solutions. Compared to aqueous standards the signal of platinum in hydrochloric acid decreases by 7–35% depending on its concentration. For 2 mol/l HCl (chosen eluent concentration) the platinum signal decreases approximately by 20%. Probably, volatile chlorocomplexes of platinum are formed and released from the graphite furnace before the atomization step. In the presence of ammonia solution in the concentration range 0.25–3 mol/l, the platinum signal decreases by 4–30%, depending on ammonia concentration. Addition of thiourea in the concentration range 1–10% to the platinum standard causes a slightly positive effect. The platinum signal increases compared to aqueous solution by 3–12% with increasing concentration of thiourea.

The atomization profiles of platinum for different types of sample were recorded (Figure 3) and indicate differences in the atomization process in the presence of thiourea. The platinum signal is shifted towards higher temperatures, probably due to the formation of stable but volatile species of the MeS type [20]. The calibration graphs for the different standards investigated were found to be linear in the range of platinum concentrations from 5 to 150 ng/ml. The correlation coefficients for all graphs were in the range 0.9987 – 0.9996. The detection limits, characteristic masses and measurement precision of platinum (n=11) by GFAAS were calculated and are given in Table III. From these data it is apparent that the preconcentration procedure is necessary for the determination of platinum in environmental samples.

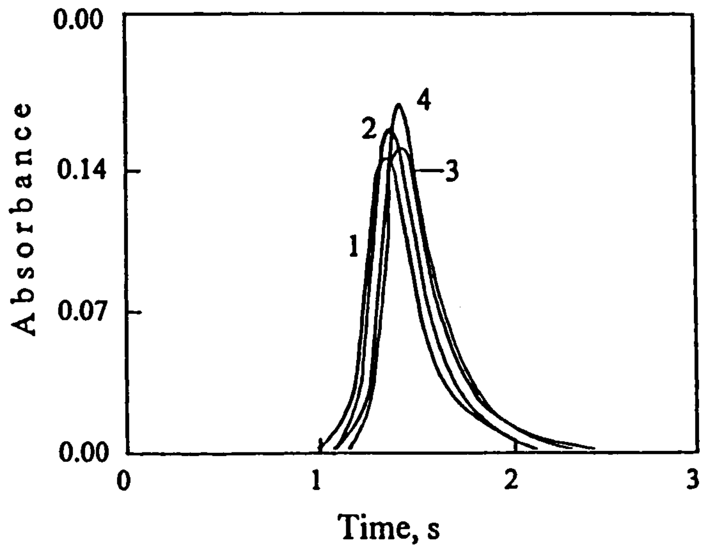

FIGURE 3 Absorbance profiles of platinum (0.6 ng) from different eluents 1- aqueous solution. 2- 2.0 mol/l NH_3 3- 2.0 mol/l HCl 4- 1.2 mol/l thiourea

TABLE III Detection limits and precision for determination of platinum in different matrices by GFAAS method (n=11)

Sample	*Characteristic mass[pg]*		*Detection limit [ng/ml]*	*Precision [%] (n=11)*
	A_h	A_{int}		
Aqueous Pt standard	20.0	66.8	2.3 (46 pg)	3.0
Pt in 2.0 mol/l NH_3	24.4	79.3	6.1 (122 pg)	3.3
Pt in 2.0 mol/l HCl	18.7	63.0	3.4 (68 pg)	3.3
Pt in 1.2 mol/l thiourea	11.0	50.6	1.6 (32 pg)	1.8

Coupling of preconcentration and determination steps

The suitability of the proposed method was checked by spiking Milli-Q water with 0.29 µg/ml of platinum (as $PtCl_6^{2-}$) for on-line preconcentration with FAAS detection and spiking Milli-Q and tap waters with 5 ng/ml of platinum for off-line preconcentration with GFAAS detection. Preconcentration was carried out on the microcolumn filled with alumina. The aqueous samples were equilibrated overnight with the platinum standard solution. The recovery and precision results (n=5) are given in Tables II and IV. The obtained detection limits of platinum at the level of several pg/ml are by about one order of magnitude lower than those reported previous by [12,13,16].

TABLE IV Analytical results for platinum preconcentration in optimized conditions on microcolumn filled with alumina sorbent and detection by GFAAS technique, (n=5)

Parameter	*MQ water spiked with 50 ng of Pt*	*Tap water spiked with 50 ng of Pt*
Precision as RSD (in %)	2.7	3.1
Recovery (in %)	106.5 ± 2.4	91.8 ± 2.8

CONCLUSIONS

The experiments performed demonstrate that platinum may be quantitatively adsorbed and preconcentrated on all tested weak anion-exchange sorbents and eluted in one small fraction. The platinum sample is adsorbed on the resins at pH 2.5–3, which is very useful, when initial mineralization procedure of environmental sample is necessary. The comparison of different resins has shown that the best enrichment factor of platinum (equal 400) was obtained when platinum was eluted with 2 mol/l ammonia solution from alumina microcolumn. However, in the case of environmental material analysis we expect better performance on Cellex-T, due to its highest capacity.

On-line microcolumn preconcentration and FAAS detection have provided a simple and rapid method for analysis of platinum at the µg/l level, whereas the off-line analysis with GFAAS detection is suitable for determination of platinum at ng/l level. The influence of different eluents on sensitivity and detection limit of platinum by GFAAS was investigated. The chosen eluents do not restrict the determination step by this technique.

The good recovery of platinum and low detection limit obtained for platinum determination in tap water shows the potential usefulness of the proposed procedure for environmental analysis.

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