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# Factorial design for multivariate optimization of an on-line preconcentration system for platinum determination by ultrasonic nebulization coupled to inductively coupled plasma optical emission spectrometry

S. Cerutti [a,b], J.A. Salonia [a], S.L.C. Ferreira [c], R.A. Olsina [a,b], L.D. Martinez [a,b,*]

[a] *Department of Analytical Chemistry, Faculty of Chemistry, Biochemistry and Pharmacy, National University of San Luis, Chacabuco and Pedernera, P.O. Box 375, 5700 San Luis, Argentina*
[b] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Rivadavia 1917, CP C1033 AAJ, Ciudad de Buenos Aires, Argentina*
[c] *Universidade Federal da Bahia, Instituto de Química, Grupo de Pesquisa em Química Analítica, Campus Universitário de Ondina, Salvador, Bahia 40170-290, Brazil*

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**Abstract**

A system for on-line preconcentration and determination of platinum by ultrasonic nebulization (USN) coupled to inductively coupled plasma optical emission spectrometry (ICP-OES) was studied. It is based on the chemical sorption of platinum on a column packed with polyurethane foam loaded with thiocyanate reagent. The optimization step was carried out using two level full factorial design. Three variables (pH, loading flow rate (LFR) and eluent concentration) were regarded as factors in the optimization. Results of the two level factorial design $2^3$ with three replicates of the central point for platinum preconcentration, based on the variance analysis (ANOVA), demonstrated that the factors and their interactions are not statistically significant. The proposed procedure allowed the determination of platinum with a detection limit of 0.28 $\mu g\,l^{-1}$. The precision for 10 replicate determinations at 10.0 $\mu g\,l^{-1}$ Pt level was 3.8% relative standard deviation (R.S.D.), calculated from the peak heights obtained. A total enhancement factor of 100 was obtained with respect to ICP-OES using pneumatic nebulization (10 for USN and 10 for preconcentration). A sampling frequency of 50 samples per hour was obtained. The effect of other ions in concentrations agreeing with water samples was studied. The addition/recovery experiments in the samples analyzed demonstrated the accuracy and applicability of the system developed for platinum determination in spiked water samples.


*Keywords:* On-line preconcentration; Factorial design; Platinum; Polyurethane foam; ICP-OES

## 1. Introduction

The determination of traces and ultra-traces of platinum in the environment, as well as in body fluids of living species, at low concentrations is an urgent problem [1–5]. Pt affects the environment to an increasing degree as pollution, especially by the technical use of catalysts containing active Pt metal. The use of catalytic converters has led to an anomalous increase in the concentrations of platinum in several natural matrices such as soil, water and vegetation, in areas near to intensive vehicle traffic, thus causing a new environmental risk [6–8]. A critical evaluation of possible risks for human health can only be given if reliable analytical data are available.

The determination of platinum at low levels requires sensitive analytical techniques, among them, flame atomic absorption spectrometry (FAAS) [9,10], electrothermal atomic absorption spectrometry (ETAAS) [11–13], inductively coupled plasma optical emission spectrometry (ICP-OES) [14,15], inductively coupled plasma-mass spectrometry (ICP-MS) [16–20], neutron activation analysis (NAA) [21,22] and capillary electrophoresis (CE) [23,24]. 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.

* Corresponding author. Fax: +54-2652-430224.
*E-mail address:* ldm@unsl.edu.ar (L.D. Martinez).

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Various methods have been developed for platinum separation and preconcentration from diverse matrices such as, anion exchange [11,20,21,25], precipitation [8,13], cloud point extraction [19], biosorption [12], co-precipitation [26] and sorption [10,14,15,27–29], among others.

Polyurethane foam (PUF) was proposed as sorbent by Bowen [30] in 1970 and has been used in many procedures for separation and preconcentration of a wide variety of inorganic and organic compounds. Braun et al. [31,32] and Palágyi and Braun [33] have described reviews about this sorbent. Unloaded PUF was recently introduced in on-line separation and preconcentration systems [34,35]. Application of PUF in these produces smaller resistance for fluid passage than materials often employed for this proposal. Thus, it results low overpressure in the system reducing risk of leakage. PUF is easily disposable, very low cost and simple preparation. Moreover, this sorbent is resistant to rough changes on pH conditions, despite to swell when in presence of some organic solvents concentrated, as ethanol. In procedures for platinum determination, PUF has been employed several times [28,29,36,37]. However, all these works has been developed in a batch mode, which involve tedious and delayed steps.

On the other hand, the optimization of analytical procedures by multivariate techniques [38–40] is faster, more economical and effective than the traditional "one-at-a-time." The multivariate optimization makes possible to understand circumstances that are not explained by the traditional approach, for example, the interactions between the factors that influence the analytical response. These advantages have been reported in the literature [41].

In this paper, factorial design was applied for optimization of the experimental variables of a simple on-line preconcentration system for platinum determination in spiked water samples. It was based on solid-phase extraction of platinum as thiocyanate complex onto polyurethane foam. The determination was carried out using ultrasonic nebulization (USN) coupled to inductively coupled plasma optical emission spectrometry (USN-ICP-OES).

## 2. Experimental

### 2.1. Reagents

Platinum (IV) standard solution was prepared by appropriate dilutions of a 1000 mg $l^{-1}$ stock solution (Fluka, Switzerland) immediately before use. The platinum solution's pH was adjusted with hydrochloric acid solution.

The hydrochloric acid was Suprapure (Merck, Darmstadt, Germany). Hydrochloric acid (0.1 mol $l^{-1}$) was prepared by direct dilution with ultrapure water from the concentrated suprapur solution.

A $1 \times 10^{-2}$ mol $l^{-1}$ potassium thiocyanate solution was prepared by dissolving the reagent in water. Lower concentrations were prepared by serial dilution in water.

Flexible polyurethane foam (PUF), commercial open-cell polyether-type polyurethane foam (by Mortimer of Argentina), was ground in a domestic blender with a large amount of ultrapure water, as previously described [42,43]. Afterwards, PUF was filtered in a vacuum system and squeezed between clean sheets of filter paper. So, PUF was placed to dry in a stove at 80 °C for 1 h and stored in a dark bottle.

Ultrapure water (18 MΩ $cm^{-1}$) was obtained from an EASY pure RF (Barnstedt, Iowa, USA). All other solvents and reagents were of analytical-reagent grade or better, and the presence of platinum was not detected in the working range.

### 2.2. Apparatus

The measurements were performed with a sequential ICP spectrometer (Baird, Bedford, MA, USA, ICP2070). The 1 m Czerny–Turner monochromator had a holographic grating with 1800 grooves $mm^{-1}$. The FI system used is shown in Fig. 1. An ultrasonic nebulizer, U 5000 AT (CETAC Technologies, Omaha, NE, USA), with desolvation system was used. The ICP and ultrasonic nebulizer operating conditions are listed in Table 1. A Minipuls 3 peristaltic pump (Gilson (Villiers-Le-Bell, France)) was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. A laboratory-made microbore glass column (50 mm length, 3.0 mm internal diameter) was used as the polyurethane foam holder. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent and eluent. The 214.423 nm spectral line was used and FI system measurements were expressed as peak-height emission, which was corrected against the reagent blank.

### 2.3. Column preparation

The $1 \times 10^{-4}$ mol $l^{-1}$ potassium thiocyanate solution was percolated through a laboratory-made column containing about 0.05 g of polyurethane foam at a flow rate of 2.5 ml $min^{-1}$ for 5 min. Afterwards, the column was washed with a 8% (w/v) sodium hydroxide solution in order to remove the excess of thiocyanate. Then, the column was

Table 1
ICP and ultrasonic nebulizer instrumental parameters

| | |
|---|---|
| ICP conditions | |
| RF generator power (kW) | 1.0 |
| Frequency of RF generator (MHz) | 40.68 |
| Outer gas flow rate (l $min^{-1}$) | 8.5 |
| Auxiliary gas flow rate (l $min^{-1}$) | 1.0 |
| Observation height (mm) | 15 |
| Ultrasonic nebulizer conditions | |
| Heater temperature (°C) | 140 |
| Condenser temperature (°C) | 4 |
| Carrier gas flow rate (l $min^{-1}$) | 1 |

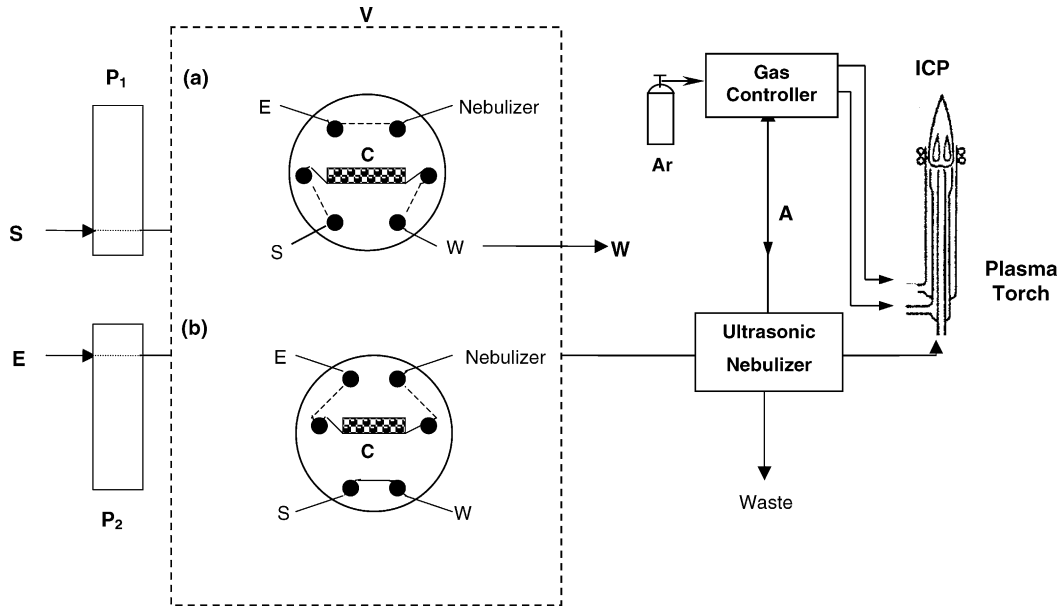


Fig. 1. Schematic diagram of the instrumental setup. S: sample (flow rate: 10 ml $min^{-1}$); E: eluent (flow rate: 1.5 ml $min^{-1}$); A: Ar (flow rate: 0.7 l $min^{-1}$); W: waste; $P_1$, $P_2$: peristaltic pumps; C: column; V: injection valve. Valve positions: (a) sample loading; (b) injection.

washed with 5% (v/v) nitric solution and ultrapure water, respectively, in order to prevent any metal contamination. The average lifetime of column is more than 300 cycles.

The column was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system.

All columns prepared by this way shown good reproducibility. It was proved by precision of the signals obtained for different columns.

### 2.4. Sample preparation

The tap water samples were filtered through 0.45 μm pore size membrane filters immediately after sampling, and were adjusted to pH 2.0 with hydrochloric acid solution and stored at 4 °C in bottles (Nalgene; Nalge, Rochester, NY, USA).

All the glassware and plasticware used were previously washed with a 10% (v/v) $HNO_3$/water solution and then with ultrapure water.

### 2.5. Preconcentration step

The solution containing platinum (standard solutions or samples) at a flow rate of 10.0 ml $min^{-1}$, adjusted to pH 2.0 with hydrochloric acid solution, was passed through a column. Platinum was retained by chemical sorption as platinum–thiocyanate complex and the remaining solution was discharged; valve V in load position (a) (Fig. 1). Finally, the peristaltic pump $P_1$ was stopped, the injection valve V was switched to the injection position (b) and the retained metal was eluted with 0.3 ml of 10% nitric acid at a flow rate of 1.5 ml $min^{-1}$, directly in the ultrasonic nebulizer and ICP-OES. The operating system measurements were expressed as peak-height emission, which was corrected against the reagent blank.

Table 2
Recovery study (tap water) (95% confidence interval; $n = 6$)

| Aliquots | Quantity of Pt added (μg $l^{-1}$) | Quantity of Pt found (μg $l^{-1}$) | Recovery (%) |
|---|---|---|---|
| 1 | 5.0 | 4.9 | 98.0 |
| 2 | 10.0 | 9.7 | 97.0 |
| 3 | 15.0 | 15.1 | 100.7 |
| 4 | 20.0 | 19.0 | 95.0 |
| 5 | 25.0 | 24.5 | 98.0 |

### 2.6. Method validation

Certified Reference Material of Natural Water with a certified value for Pt do not exist, and due to the method of standard addition is considered as a validation method [44], then in order to demonstrate the validity of this method, 50 ml of tap water was collected and divided into five portions of 10 ml each. Then, increasing quantities of platinum were added to the aliquots of sample and platinum was determined by means of the preconcentration method (Table 2).

## 3. Results and discussion

### 3.1. Experimental conditions

The optimization step of the proposed procedure was performed using a full factorial design ($2^3$) with (3) replicates of the central point, involving the variables: pH, loading flow

Table 3
Factors and levels used in factorial design

| Variable | Low (−) | Central point (0) | High (+) |
|---|---|---|---|
| pH | 1.0 | 2.0 | 3.0 |
| LFR (ml min$^{-1}$) | 3.5 | 7.0 | 10.0 |
| Eluent concentration (EC) (%) | 5.0 | 10.0 | 15.0 |

Table 4
Design matrix and results of the factorial design

| Experiment | pH | LFR | EC | RR (%)[a] |
|---|---|---|---|---|
| 1 | + | + | + | 70.8 |
| 2 | + | + | − | 80.6 |
| 3 | + | − | + | 100.0 |
| 4 | + | − | − | 71.4 |
| 5 | − | + | + | 83.3 |
| 6 | − | + | − | 67.8 |
| 7 | − | − | + | 93.8 |
| 8 | − | − | − | 74.5 |
| 9 | 0 | 0 | 0 | 82.1 |
| 10 | 0 | 0 | 0 | 82.1 |
| 11 | 0 | 0 | 0 | 81.3 |

[a] Relative response (%).

rate (LFR), and eluent concentration (EC) and the ICP-OES signal as analytical response (the experimental data were processed by using the Statistic computer program). Minimum and maximum levels of each factor (Table 3) were chosen according to data from previous experiments. Table 4 shows the experimental design matrix and the analytical signal, the relative response (%) was calculated taking the maximum value obtained as 100%; and the remaining values showed in the table were calculated from it. The results of this study, considering the ANOVA as Table 5 and the

Table 5
Analysis of data given in Table 4

| Factor | SS[a] | DF[b] | MS[c] | *F* ratio | *P* level[d] |
|---|---|---|---|---|---|
| pH | 1.445 | 1 | 1.445 | 0.11233 | 0.925268 |
| LFR | 172.980 | 1 | 172.980 | 1.344638 | 0.365943 |
| EC | 359.120 | 1 | 359.120 | 2.791573 | 0.236717 |
| pH-LFR | 0.980 | 1 | 0.980 | 0.007618 | 0.938400 |
| pH-EC | 32.000 | 1 | 32.000 | 0.248748 | 0.667410 |
| LFR-EC | 222.605 | 1 | 222.605 | 1.730391 | 0.318925 |
| Error | 257.289 | 2 | 128.6443 | | |
| Total | 1254.043 | 10 | | | |

[a] Sum of squares.
[b] Degrees of freedom.
[c] Mean squares.
[d] Probability level.

Pareto chart (Fig. 2) demonstrate that in the studied levels, all these variables and their interactions are not statistically significant. In this way, the pH recommended is 2.0 considering that it is the central point of the pH interval tested. It guarantees the robustness of the system for this variable; the chosen LFR was 10 ml min$^{-1}$ in order to obtain a better throughput sample, and the eluent concentration selected was 10% (v/v) nitric acid.

The eluent flow rate was not considered as variable, it was fixed at 1.5 ml min$^{-1}$ as optimum flow rate of the spectrometer.

### 3.2. Interferences

The effects of potentially interfering species (at the concentration levels at which they may occur in the sample concerned) were tested under the optimal preconcentration

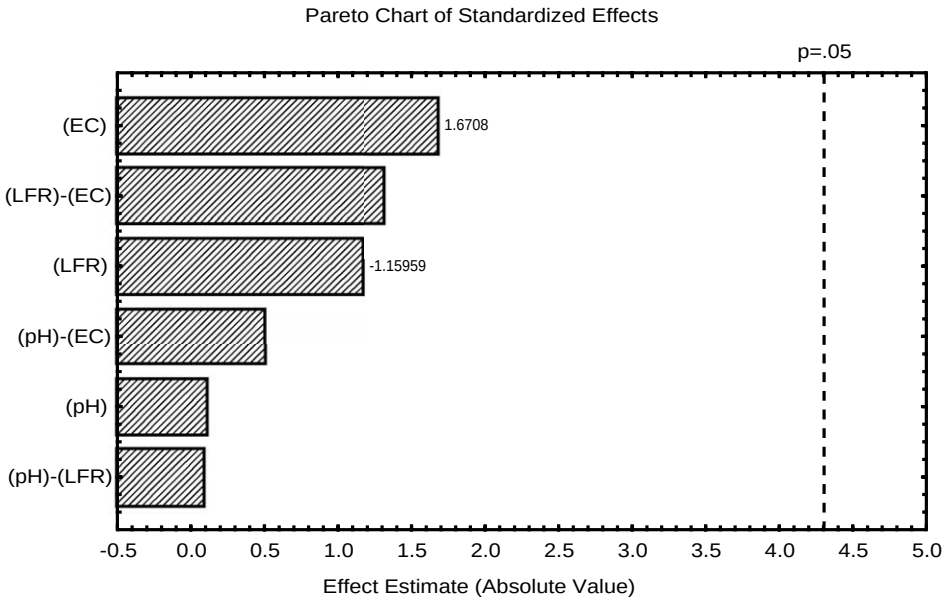


Fig. 2. Pareto chart of standardized effects for variables in the platinum preconcentration.

conditions. Thus $Cu^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Mn^{2+}$ and $Fe^{3+}$ could be tolerated up to at least 2500 $\mu g\,l^{-1}$.

### 3.3. Analytical performance

The overall time required for preconcentration of 10 ml of sample (1 min, at flow rate of 10 ml $min^{-1}$), and elution (approximately 0.2 min, at flow rate of 1.5 ml $min^{-1}$) was about 1.2 min; the throughput was about 50 samples per hour. A sensitive enhancement factor of 100 was obtained with respect to ICP-OES using pneumatic nebulization (10 for USN and 10 for preconcentration).

The precision for 10 replicate determinations at 10 $\mu g\,l^{-1}$ Pt level was 3.8% relative standard deviation (R.S.D.), calculated from the peak heights obtained. The detection limit (DL) was calculated as the concentration of platinum required to yield a net peak that was equal to three times the standard deviation of the blank signal ($3\sigma$). The value of detection limit obtained for the preconcentration of 10 ml of sample solution was 0.28 $\mu g\,l^{-1}$.

### 3.4. Application to tap water samples

Finally, the results of the method applied to platinum determination in spiked tap water samples are shown in Table 2.

## 4. Conclusions

Application of the factorial designs allowed the optimization of the preconcentration procedure, which was found to be more efficient and needs for fewer number of experiments. The developed methodology in this paper was successfully applied to the determination of platinum in spiked water samples.

The developed manifold permitted high sample flow rates in order to achieve good sensitivity. This method proved to be rapid, reliable and flexible with limited interference.

High sample throughput (50 samples per hour) is a great advantage of this procedure if compared to many methods existing to platinum preconcentration.

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