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PAPER

Factorial and Doehlert designs in the optimization of a separation procedure using polyurethane foam as a solid phase extractant for platinum determination in ferrous matrices using inductively coupled plasma optical emission spectroscopy

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A procedure for separation of platinum from ferrous matrices was developed using platinum sorption as chloride complexes on polyurethane foam, with subsequent determination by inductively coupled plasma optical emission spectrometry (ICP OES). The procedure was optimized using a two-level full factorial and Doehlert designs. Four variables (foam mass, shaking time, stannous chloride concentration and hydrochloric acid concentration) were regarded as factors in the extraction optimization. Results of the two-level full factorial design, 2^4 with 16 runs based on Analysis of Variance (ANOVA) showed that only two factors (foam mass and shaking time) are statistically significant. Doehlert design was applied in order to determine the optimum conditions for platinum separation. The proposed procedure allowed platinum determination with a detection limit of 66 μg L^{-1} and a precision, calculated as relative standard deviation (RSD), of 1.2% in a set of 10 measurements for a platinum concentration of 10.0 μg L^{-1}. The studied procedure was applied to platinum determination in several ferrous matrices (iron ores, pure iron and catalysts). Spike tests on iron ores and pure iron showed good performance in platinum recovery. The good accuracy of the proposed procedure was confirmed by analysis of an ore platinum standard reference material (SARM-7).

1. Introduction

Due to its properties, such as resistance to corrosion, low malleability and high resistance to deformation, platinum is a metal with many applications in the modern world. This metal is mainly used in automobile exhaust catalytic converters and as a catalyst in a wide variety of processes such as nitric acid production and petroleum re-forming. Platinum has applications in chemical, glass and electronic component industries, as well as in the manufacture of jewelry. Some platinum coordination compounds are also used in chemotherapy for the treatment of some types of cancer.[1,2]

Platinum is an extremely rare metal in the Earth's crust and its occurrence is frequently associated with ferrous matrices. Due to the technological utilization of platinum, its quantification is increasingly necessary and also to evaluate its environmental impact.[3] The determination of platinum requires analytical techniques with adequate sensitivity like Flame Atomic Absorption Spectrometry (FAAS),[4,5] Electrothermal Atomic Absorption Spectrometry (ETAAS),[6,7] Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES),[8] Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)[9,10] and Neutron Activation Analysis (NAA).[11]

Even though ICP OES is an efficient alternative for platinum determination, this task becomes difficult when it comes to high ferrous samples, due to the complex emission spectra of these matrices, causing interference in the platinum emission lines. Matrices with high iron content can cause fluctuations in the measurement of intensities, background radiation displacement and, consequently, alterations in the background equivalence concentration (BEC) and detection limit values. Thus, analytical procedures aimed at separating platinum traces from high iron content matrices are alternatives to overcome problems related to platinum determination using ICP OES.[12,13]

A separation step can be applied in order to remove the ferrous matrix interferences and thereby enable analyte determination. It has been documented in the literature that various methods have

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already been developed for platinum separation and preconcentration from environmental and biological matrices, *e.g.*, liquid–liquid extraction,[14] sorption on several solid-phases,[15–17] ionic exchange,[18] precipitation,[19] cloud point extraction,[20] biosorption,[21] co-precipitation,[22] among others.

Solid-phase extraction provides important benefits such as, simplicity, reliability, good metal loading capacity, ability to obtain high enrichment factors, economical chemicals, reutilization of the solid phase and low solvent consumed, hence making it an efficient alternative to carry out separation and preconcentration procedures.[23–25] Polyurethane foam (PUF) has been used as a sorbent in many procedures for separation and preconcentration of a wide variety of inorganic and organic compounds.[26] PUF is easy to dispose of, it is cheap and does not require complex preparation procedures. Moreover, this sorbent is resistant to extreme changes in pH, despite swelling when in the presence of some concentrated organic solvents such as ethanol.[27] This material has also been applied in the determination of platinum in tap water.[28]

In this study, multivariate techniques (two level factorial and Doehlert designs)[29] have been applied for optimization of the experimental variables of a separation procedure for the determination of platinum in ferrous matrices. The extraction procedure is based on the solid-phase extraction of platinum as a chloride complex into polyurethane foam followed by determination by ICP OES.

2. Experimental

2.1. Instrumentation

A Varian (Mulgrave, Australia) Vista simultaneous inductively coupled plasma optical emission spectrometry instrument with axial viewing and a Charge Coupled Device (CCD) as detector, equipped with a cyclonic chamber, and a pneumatic concentric nebulizer have been used. Platinum determination was carried out under the conditions recommended by the manufacturer as regards power (1.3 kW), radio frequency generation (40 MHz), plasma gas flow (15.0 L min^{-1}), auxiliary gas flow (1.5 L min^{-1}) and nebulizer gas flow (0.7 L min^{-1}). The analytical wavelength (nm) used for all determinations was 214.423 II.

2.2. Reagents and solutions

All reagents were of analytical grade, unless otherwise stated. Ultrapure water (Milli-Q®, Millipore, USA) with a conductivity value around 18.2 mΩ cm^{-1} was used in the experiments.

The platinum reference solutions were prepared from an ICP Standard 1000 mg L^{-1} stock solution (Centipur, Merck, Germany) containing hexachloroplatinic acid in 7% Suprapur® hydrochloridric acid.

In a minimal volume of concentrated HCl, an iron solution (20000 mg L^{-1}) was prepared by dissolution of 20 g of this metal, and the final volume was set to 1000.0 mL using 1 mol L^{-1} HCl.

A 35% (m/m) stannous chloride ($SnCl_2 \cdot 2H_2O$) solution was prepared on a dissolution basis of 41.64 g of reagent in 63 mL concentrated HCl, and the final volume was set to 100.0 mL with deionized water.

Laboratory glassware was kept overnight in 10% (v/v) nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in a dust-free environment.

2.3. Polyurethane foam preparation

An open cell polyether-type commercial polyurethane foam (Atol, Brazil) was ground in a domestic blender with a large amount of deionized water, as previously described.[30] Afterwards, PUF was filtered off in a vacuum system and squeezed between clean sheets of filter paper. PUF was then placed to dry in a stove at 80 °C for 1 h and stored in a dark bottle.

2.4. Sample preparation

2.4.1. Certified samples of iron ores and pure iron. The iron ore and pure iron samples were provided by IPT (Technologic Research Institute of São Paulo State, Brazil). About 1 g of the sample was weighed and treated with aqua regia (20 mL) in a beaker, and heated for dissolution and evaporation. After that, the volume was made-up to 50.00 mL with 7 mol L^{-1} HCl solution.

2.4.2 Catalysts. Catalysts provided by the Study Group in Kinetic and Catalysis (Universidade Federal da Bahia) were analyzed. In a beaker, about 0.1 g of the sample was weighed and treated with aqua regia (3 mL) and put into a pressurized digestion vessel for 4 h. After that, the volume was made-up to 50.00 mL with 1% (m/v) HCl solution.

2.4.3. Standard reference material. For digestion of the Certified Reference Material (CRM) of platinum ore (SARM-7, South Africa), a digestion method adapted from studies conducted by Brooks and Lee[31] and Simonsen[32] was used. The adapted method is described below:

The CRM was dried between 100–110 °C for 2 h. After that, 5 g of the sample was put into a muffle furnace at 600 °C for 2 h. After cooling down, the samples were transferred to a Teflon® beaker, and 5.00 mL of concentrated nitric acid and 25.00 mL of fluoridric acid 40% the beaker was heated on a hot plate until the solution evaporated to dryness. A total of 25 mL of aqua regia was added and the beaker was covered and heated at 95–100 °C for 2 h. Then, the cover was removed and the mixture was left to dry. Next, 6 mol L^{-1} hydrochloric acid was added and the mixture was again left to dry. After that, 6 mol L^{-1} hydrochloric acid was added and the sample was heated for salt dissolution. After cooling, the mix was transferred into a centrifuge tube. Immediately after centrifugation, the liquid phase was carefully removed from the tube and stored in a polyethylene flask followed by the separation procedure. The solid residues that remained in the centrifuge tube were thrice submitted to washing using 1 mol L^{-1} hydrochloric acid (5 mL) and put into a storage flask.

2.5. Multivariate optimization

2.5.1. Two-level factorial design. One hundred milligrams of platinum(II) were added to a synthetic ferrous matrix containing 125 μg of Fe(III) in all experiments. Initially, platinum was extracted from this ferrous matrix, in polyurethane foam, according to the experimental conditions for shaking time (ST),

Table 1 Panel A: Factors and levels used in factorial design and Panel B: two-level factorial design and the results for platinum extraction (%)

Panel A

Variable	Low (−)	Central (0)	High (+)
[HCl] (mol L^{-1})	0	0.1	0.2
PM (mg)	20	60	100
[$SnCl_2$] (mol L^{-1})	0.2	0.4	0.6
ST (min)	10	20	30

Panel B

N (°)	[HCl]	PM	[$SnCl_2$]	ST	Extraction (%)
01	—	—	—	—	20
02	+	—	—	—	8
03	—	+	—	—	44
04	+	+	—	—	39
05	—	—	+	—	14
06	+	—	+	—	13
07	—	+	+	—	40
08	+	+	+	—	42
09	—	—	—	+	42
10	+	—	—	+	48
11	—	+	—	+	48
12	+	+	—	+	48
13	—	—	+	+	48
14	+	—	+	+	52
15	—	+	+	+	54
16	+	+	+	+	52
17	0	0	0	0	65
18	0	0	0	0	62
19	0	0	0	0	63

$SnCl_2$ concentration ([$SnCl_2$]), HCl concentration ([HCl]) and polyurethane foam mass (PM) presented in Table 1a. After shaking, PUF was separated by vacuum filtration using quantitative filter paper and washed with deionized water. The solid-phase was transferred into a dry beaker, and platinum was re-extracted following the addition of 2 mL of concentrated nitric acid and 8.0 mL of demineralized water. The foam was filtered and platinum was determined in the filtrate by ICP OES. Maximum and minimum levels of each factor are presented in Table 1b.

2.5.2. Doehlert design. $SnCl_2$ and HCl solutions in concentrations indicated as optimum according to the results of factorial design were added to the synthetic ferrous matrixes containing 125 μg of Fe(III) and 100.0 mg of platinum(II). Shaking time and polyurethane foam mass were observed to vary according to experiments from the Doehlert matrix presented in Table 2. The extraction procedure was carried out as described in section 2.5.1.

Table 2 Doehlert design for optimization of the platinum separation from ferrous matrixes using polyurethane foam as solid phase

N (°)	ST (min)	PM (mg)	Extraction (%)
01	12 (−0.5)	65 (0.866)	60
02	28 (0.5)	65 (0.866)	63
03	4 (−1.0)	50 (0)	51
04	20 (0)	50 (0)	68
05	20 (0)	50 (0)	66
06	20 (0)	50 (0)	65
07	36 (1.0)	50 (0)	66
08	12 (−0.5)	35 (−0.866)	40
09	28 (0.5)	35 (−0.866)	45

2.6. Proposed procedure for platinum determination in ferrous matrices

The ferrous sample containing platinum was added to a polyethylene flask with 15 mL of 0.4 mol L^{-1} $SnCl_2$, 3.0 mL of 0.1 mol L^{-1} HCl and 60 mg of polyurethane foam. The flask was mechanically shaken for approximately 30 min. The extraction procedure was carried out as described in section 2.5.1. Platinum was determined in the filtrate by ICP OES, using the Pt II 214.423 nm line.

3. Results and discussion

3.1. Adsorption mechanism

The adsorption of Pt–Sn(II) complexes on the polyurethane foam in HCl media has been investigated by Schroeder and Chow.[33] The chemical species $SnCl^{3-}$ increases the interaction of the platinum complex with the foam surface and thereby its adsorption. The cation chelation mechanism showed that the absorption of complexes on polyurethane foam depends on its functional groups and also on the radius of cations associated with the layers of anionic counter-ions present in the aqueous solution. According to this mechanism, the counter-ions are effectively solvated by the oxygen atoms of the polyethylene oxide portion of foam, forming chelates similar to complexes with crown ethers. These polymer sections form a helical structure with oxygen atoms directed inward, thus defining cavities that improve cation selectivity for the formation of protonated sites in the PUF.

3.2. Choice of eluent

Several eluents (CH_3COOH, HCl, HNO_3 and NH_4Cl) at different concentrations were evaluated as platinum extractors from polyurethane foam. The nitric acid solution (3.2 mol L^{-1}) showed the best performance, allowing obtaining extractions of about 65%.

3.3. Optimization of the procedure

3.3.1. Two-level factorial design. A full two-level factorial design was used in the screening study. The results are summarized in Table 1b and the variable referring to significance can be evaluated using the Pareto chart (Fig. 1). The Pareto chart shows the effects sorted by their absolute size. There is a vertical line to indicate the minimal magnitude of statistically significant effects, allowing for the simultaneous review of a large number of factors and for the extraction of information about the system. The evaluation demonstrates that the two studied factors are statistically significant (shaking time and polyurethane foam mass) and require a final optimization. According to the positive estimated effect for shaking time and polyurethane foam mass, their increase allows the platinum extraction process to be improved; yet, this linear mathematical model does not establish a practical limit, which can only be determined using the Doehlert design. Moreover, $SnCl_2$ and HCl concentration factors do exert a significant effect inside the studied experimental region and must have their values fixed at a focal/critical point in the next step for optimization. The Pareto graph also shows that

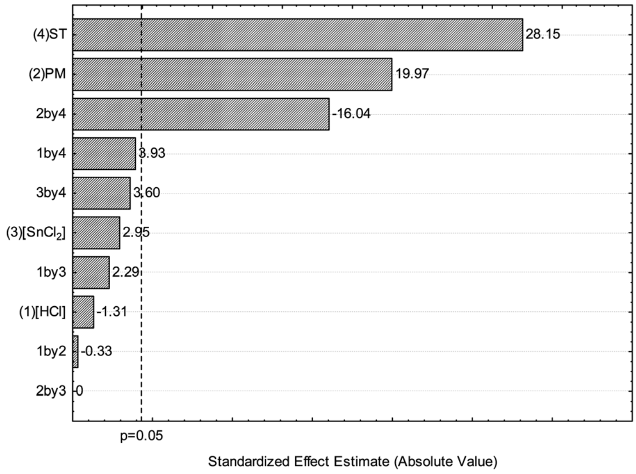

Fig. 1 Pareto chart for the full factorial design. Dashed line represents the limit to significant values according to a confidence interval of 95%.

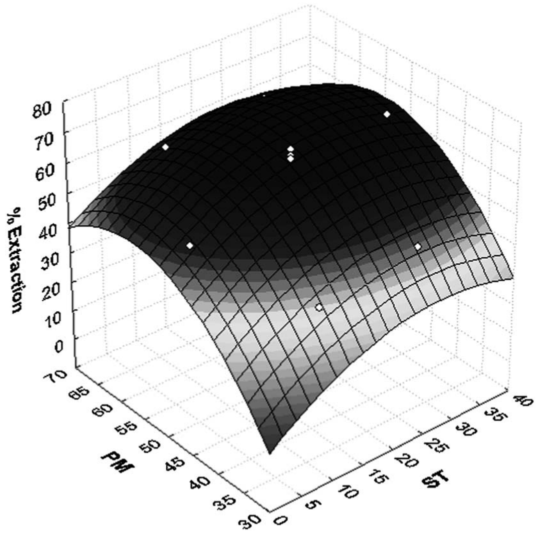

Fig. 2 Response surfaces for shaking time (ST) *versus* polyurethane foam mass (PM).

interactions between shaking time and polyurethane foam mass exert a significant effect. These interactions are evidence of the synergic effect between this pair of variables, which will be selected for further optimization. Hence, the application of the Doehlert design is essential in order that the localization of optimum values of two variables exerting significant effect becomes feasible.

3.3.2. Doehlert design. A Doehlert matrix for two variables was applied in order to find the optimum conditions for shaking time and polyurethane foam mass. In this procedure, $SnCl_2$ and HCl concentrations were fixed at 0.4 and 0.1 mol L^{-1}, respectively. The experimental results obtained using the Doehlert design for these variables along with the coded and real values for the studied variables are shown in Table 2.

The equation below was obtained after fitting a quadratic function to data from Table 2; it illustrates the relationship of these two variables and the response (*R*), where *R* stands for the recovery rate observed after the preconcentration procedure.

$$R\ (\%\text{ext}) = -127\ (\pm 14) + 1.8\ (\pm 0.4)\ \text{ST} - 0.031\ (\pm 0.005)\ \text{ST}^2 + 6.2\ (\pm 0.5)\ \text{PM} - 0.055\ (\pm 0.005)\ \text{PM}^2 - 0.004\ (\pm 0.006)\ \text{ST*PM}$$

The corresponding surface response is shown in Fig. 2. Lagrange criteria [34] applied to this equation indicates that the critical point is characterized as a maximum.

In order to assess the model fitness, analysis of variance (ANOVA) was applied to experimental data model fitness (Table 3). A lack of fit test shows that the calculated *F* (3.50) < Tabulated *F* (18.51), thus indicating that there was good agreement between the model's predicted response (% extraction) and the experimental values studied for each variable.

The derivatization of this general equation as ST and PM results in two new equations:

$$\frac{\delta R}{\delta \text{ST}} = 1.8 - 0.062\text{ST} - 0.004\text{PM} = 0$$

$$\frac{\delta R}{\delta \text{ST}} = 6.2 - 0.004\text{ST} - 0.110\text{PM} = 0$$

The critical values for the variables can be found by solving these equation systems. Thus, critical values were 26 min (shaking time) and 56 mg (polyurethane foam mass). These values were therefore established as optimal conditions for this method.

As can be observed from Table 2, the increasing of polyurethane foam mass (and thereby the number of adsorption sites available) does not improve the percentage extraction of platinum. As quantitative recoveries are observed in the absence of ferrous matrix, this is an indication that it interferes with the extraction. Then, in order to eliminate its effects, the solutions forming the calibration curve must be submitted to the same steps as for the sample extraction.

3.4. Analytical features of the procedure

The analytical characteristics of the proposed procedure using a bath solid-phase extraction for platinum separation from ferrous matrices and determination by ICP OES were accessed. All analytical parameters were obtained using a synthetic ferrous matrix containing 125 µg of Fe(III).

Because the extraction results are not quantitative under the optimum conditions (reaching about 68%), platinum determination was carried out by submitting the solutions of the calibration curve to the same extraction procedure applied to the samples. The concentrations of the standards proposed for construction of the analytical curves ($n = 5$) ranged from 2.5 to 20.0 µg mL^{-1}. The detection limit was calculated as ($3s\ S^{-1}$), where *S* refers to the slope of the analytical curve and *s* stands for the standard deviation of ten consecutive measurements of the blank, which were found to be 66 µg L^{-1}. The precision of the procedure evaluated as relative standard deviation (RSD) and obtained after analyzing a series of 10 replicates was 1.2% for a platinum concentration of 10.0 mg mL^{-1} in the ferrous matrix.

The method accuracy was evaluated by analysis of an ore platinum standard reference material (SARM-7). Comparison of results obtained by the proposed method (3.94 ± 0.08) and the

Table 3 Analysis of variance for the quadratic model fitted to response (% extraction) obtained from Doehlert design application[a]

Source of variation	SS	df	MS	Calculated *F*	Tabulated *F*
Model	834.7222	5	166.9444	39.0258	9.01
Residual	12.8334	3	4.2778		
Lack of fit	8.1667	1	8.1667	3.5000	18.51
Pure error	4.6667	2	2.3333		
Total	847.5556	8			

[a] SS, Sum of square; df, degree of freedom; MS, median of square.

certified value (3.74 ± 0.04), using analysis of variance between groups, confirms its accuracy ($p = 0.1137 > 0.05$).

3.5. Application

The optimized methodology was applied to determine platinum concentration from samples with high iron content, such as catalyzers, iron ore and pure iron. Catalyzers consisted of 0.4% platinum supported in alumina and contaminated with 1.000 µg mL^{-1} Fe(III) solution. The catalyst samples were supplied by the "Grupo de Estudos em Cinética e Catálise" (GECCAT) from Universidade Federal da Bahia, Brazil. Iron ore (IPT -21A, IPT-27A and IPT-23A) and pure iron (IPT-73) were supplied by the "Instituto de Pesquisas Tecnológicas" (IPT, a Brazilian Research Institute). The four analyzed catalyst samples presented platinum contents ranging from 4149 to 4328 µg g^{-1}. As IPT samples present platinum contents below the limit of quantification of this method, platinum was added to a final concentration of 2 µg g^{-1} before the method was applied. Recoveries of 98 to 102% were obtained for these samples.

4. Conclusions

The application of factorial designs and Doehlert matrix allowed the efficient optimization of a procedure based on solid-phase extraction using polyurethane foam as a sorbent. The methodology is trustworthy and allows platinum separation, making it suitable for ferrous sample analysis by ICP OES. The achieved platinum concentration in the certified reference material was consistent with the reported values, confirming the method's accuracy. Results from analysis of catalysts, spiked iron ore and pure iron have shown that the developed method could be successfully applied in the determination of platinum content from ferrous samples.

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