Articles

Orthogonal Array Design for the Optimization of Supercritical Carbon Dioxide Extraction of Different Metals from a Solid Matrix with Cyanex 301 as a Ligand

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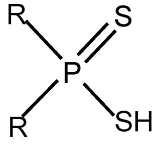
In this study, different metal cations such as Ag^+, Pd^{2+}, Mn^{2+}, In^{3+}, Au^{3+}, and Bi^{3+} were removed from a solid matrix using supercritical CO_2 containing cyanex 301 as a ligand. When the solvating power of supercritical CO_2 is combined with the metal ion complexing power of an organic ligand, a clean alternative to conventional liquid−liquid and liquid−solid extraction is obtained. An orthogonal array design (OAD), OA_9 (3^4), was employed as a chemometric method for the optimization of the supercritical fluid extraction (SFE) of metal cations from a solid matrix. Four parameters, namely, the pressure and temperature of the supercritical fluid, the dynamic extraction time, and the volume of modifier, were studied and optimized by a three-level OAD in which the interactions between the parameters were temporarily neglected. To optimize the SFE condition for each cation, nine experiments were performed in random order. Determinations of the extracts were performed by atomic absorption spectroscopy. The effects of parameters were studied using analysis of variance (ANOVA). The results showed that Ag^+, Pd^{2+}, Mn^{2+}, In^{3+}, Au^{3+}, and Bi^{3+} could be effectively extracted from the solid matrix by using supercritical fluid extraction and cyanex 301 as a chelating agent. Finally, the experimental conditions providing the highest extraction yield inside the experimental domain considered were proposed.

Introduction

Chelation combined with solvent extraction is one of the most widely used techniques for the preconcentration and separation of metal ions from aqueous samples for analytical purpose.[1] These solvent extraction procedures, however, are usually time-consuming, especially for solids where leaching procedures are needed to release the metal ions before complexation and solvent extraction. In many cases, solvent extraction requires the use of toxic organic liquids, generating environmental problems for the handling and disposal of used solvents.[2,3]

Supercritical CO_2 extraction is one promising substitute for metal-extraction media because of relatively high sample throughput, high selectivity, simplification and reduction of both solvent usage and solvent waste generation, faster extraction rates, higher extraction efficiency for shorter extraction times than for liquids, and the ability to couple to other separation techniques (GC, SFC, and LC).[4−6] In this technique, carbon dioxide is used at its critical state, which flows with low viscosity and penetrates the solid matrix. It dissolves and carries the analytes from the sample to a trap containing small amounts of solvent. Carbon dioxide is readily available, inexpensive, nontoxic, nonflammable, and chemically inert under many conditions. It is environmentally acceptable, liquefiable at reasonable pressures, economical, and easily recyclable.[7−10] The direct extraction of metal ions with supercritical CO_2 is not possible because of the charge neutralization requirement and the weak solvent−solute interaction.[1,11] One approach for extracting metal ions with supercritical CO_2 is to convert the charged metal species into neutral metal chelates by using a suitable ligand dissolved in the fluid phase.[12] The selection of a suitable chelating agent is critical in the chelation SFE of metal ions. Important requirements include high stability constants of the metal complexes, fast complexation kinetics, high solubilities of the chelating agents and their metal complexes in pure or modified supercritical carbon dioxide, and complexing specificity to allow the selective extraction of a metal ion or a group of metal ions.

A variety of organic complexing agents, such as dithio carbamates, β-diketones, crown ethers, sodium bis(trifluoroethyl)dithiocarbamate, TBP, TBPO, TOPO, TPPO, and dichloro-bis(triphenyl phophine) have been used in SFE of metal ions.[2,13] The present study demonstrated that supercritical CO_2 modified with cyanex 301 is a suitable solvent for extracting Pd^{2+}, In^{3+}, Bi^{3+}, Ag^+, Au^{3+}, and Mn^{2+} ions from solid samples. Cyanex 301 has the following structure:



where R = $(CH_3)_3C-CH_2-CH(CH_3)-CH_2-$.

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Table 1. Assignment of the Factors and Levels of the Experiments by Using an OA_9 (3^4) Matrix[a]

run no.	P/atm	T/K	t/min	M/v/v%
1	100	308	10	0
2	100	318	15	5
3	100	328	20	10
4	200	308	15	10
5	200	318	20	0
6	200	328	10	5
7	300	308	20	5
8	300	318	10	10
9	300	328	15	0

[a] Four parameters were optimized: pressure (P/atm), temperature (T/K) of supercritical fluid, dynamic extraction time (t/min) and percentage of modifier (M/v/v %).

Cyanex 301 is one of the frequently used ligands in the supercritical CO_2 extraction of metal species. It is commercially available and able to extract simultaneously more than 40 species of metal ions from aqueous solutions. It has high solubility in supercritical carbon dioxide.[13]

In the present study, orthogonal array designs[14] were used to optimize the supercritical fluid extraction conditions. The effects of pressure, temperature, and dynamic extraction time and modifier volume on the extraction efficiencies of metal ions from solid matrixes were studied by a three-level orthogonal array design with an OA_9 (3^4) matrix without considering the interactions between the parameters.

Experimental Section

Materials. Analytical-grade bis-(2,4,4-trimethyl pentyl)-dithiophosphinic acid (cyanex 301) from Fluka was used as received. HPLC-grade dichloromethane and methanol were purchased from Aldrich. Au(III), Pd(II), Bi(III), Mn(II), In(III), and Ag(I) working solutions were prepared by appropriate dilution of 1000 μg mL^{-1} stock standard solutions (Merck). No. 1 Whatman filter paper (Whatman, Maidstone, U.K.) was used in all extractions. Pure carbon dioxide (Sabalan, Tehran, 99.99%) was used for all extractions as a solid matrix.

Apparatus. A Suprex MPS/225 system (Pittsburgh, PA) in SFE mode was used for all of the extractions. In this study, extractions were accomplished with a 1-mL-volume extraction vessel. A home-built stainless steel restrictor with an appropriate flow rate was used to maintain the extraction pressure. To prevent sample plugging, the restrictor point was warmed electrically. All absorbance measurements were carried out with a Perkin- Elmer model 560 atomic absorption spectrometer under the recommended conditions for each metal ion.

Sample Preparation. For sample preparation, the solid matrix was spiked with metal ions according to the following procedure: a filter paper spiked with 100 μL of 1000 μg mL^{-1} aqueous solutions of the appropriate metal ions. The filter paper was dried at room temperature. After mixing the spiked solid matrix with 20 mg of the pure ligand, which corresponds to about 6.24 × 10^{-2} mmol of the cyanex 301, the mixture was placed in the extraction vessel.

Procedure. SFE extractions were carried out by using a combination of a 15-min static extraction (for enhancing sample−extractant contact, thus favoring the attainment of portion equilibrium) followed by 10-, 15-, and 20-min dynamic extraction steps (in which the extractant passed continuously through the extraction chamber, thus displacing the equilibrium quantitatively). Restrictor and trap temperatures were held constant by an electrical heater and an ice bath, respectively, during the extraction step. The flow rate of the supercritical fluid in the dynamic extraction step was fixed at 0.5 mL min^{-1} (compressed). To optimize the SFE procedure, an experimental design approach was followed. The variables (pressure, temperature, dynamic extraction time, and modifier volume) were as shown in Table 1. Extracts were collected in about 3 mL of dichloromethane in 5-mL vials. The collection efficiency was determined by evaporation of the samples collected in dichloromethane at ambient temperature, and the residue was dissolved in methanol and then diluted to 5 mL with methanol. The concentration was then determined by atomic absorption spectroscopy. The collection efficiency was calculated with the equation

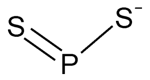
$$\% \text{ collection efficiency} = \frac{\text{mass of metal collected}/\mu\text{g} \times 100}{\text{mass of metal loaded}/\mu\text{g}}$$

The blank solution was prepared similarly to those described above for the samples.

Results and Discussion

Optimization is an important step in developing a supercritical fluid extraction method. Two general systematic optimization procedures are simultaneous and sequential methods.[15,16] In sequential methods (e.g., simplex optimization), the response surface is sequentially tracked until an optimum has been located.[17] Disadvantages of sequential methods are slow convergence on the complex response surface and difficulty in dealing with the response surface with high dimensionality. The methods may be suitable as a means for fine tuning a separation.[18] However, the simultaneous optimization methods, such as mixture designs[7,19] and factorial designs,[20−30] do not suffer from these problems.

Supercritical Fluid Extraction. The cyanex 301 show the capability to extract all of the metals studied in quantitative amounts;[13] the active region in this ligand for metal complexation is the functionality



This reagent has been shown to be good general reagent for the extraction of heavy metals using conventional solvent extraction. The aim of this work was to find the conditions providing the highest SFE recoveries of interesting metal ions and estimate the results under optimum conditions.

Because various parameters potentially affect the SFE process, the optimization of the experimental conditions represents a critical step in the development of an SFE method. In fact, the solubility of the analytes can be controlled by the composition, density, and temperature of the extraction fluid; however, the extraction recovery is dependent not only on the operating parameters but also on sample characteristics (water content, type of matrix, particle size, etc.), making the selection of optimum conditions required for subsequent reliable quantification difficult.

In this work, the effects of four parameters (pressure and temperature of the supercritical fluid, dynamic extraction time and volume of the methanol as a modifier) on the extraction of some metal ions from the solid matrix were investigated by using an experimental design.

Table 2. Results of the Effects of Selected Variables on the Extraction Efficiency

trial no.	metal cation					
	Ag^+	Pd^{2+}	Mn^{2+}	In^{3+}	Bi^{3+}	Au^{3+}
1	25.6	0.0	1.0	10.8	37.7	10.7
2	54.4	11.2	19.5	70.2	55.0	19.2
3	20.6	4.6	3.6	26.2	0.0	14.4
4	57.0	24.8	45.0	69.6	54.0	71.45
5	70.7	24.0	17.0	55.6	47.8	64.8
6	58.4	32.6	42.0	65.6	96.4	78.2
7	75.9	47.3	62.0	79.6	90.2	62.4
8	80.0	29.5	70.0	88.2	89.5	60.8
9	62.0	59.7	20.0	10.8	87.7	62.2

Table 3. Results of the Main Effects for Each Variable on the Extraction Efficiency

		average percentage of extraction					
factors	level	Ag^+	Pd^{2+}	Mn^{2+}	In^{3+}	Bi^{3+}	Au^{3+}
P/atm	100	35.5	5.3	8.0	35.7	30.9	14.8
P/atm	200	62.0	27.1	34.7	63.6	82.7	71.5
P/atm	300	72.6	45.5	50.7	59.5	89.1	61.8
T/K	308	52.8	24.0	36.0	53.4	60.6	48.2
T/K	318	68.4	21.6	35.5	71.4	80.8	48.3
T/K	328	46.7	32.3	21.9	34.2	61.4	51.6
t/min	10	54.7	20.7	37.7	54.9	74.5	49.9
t/min	15	57.8	31.9	28.2	50.2	65.6	51.0
t/min	20	55.7	25.3	27.5	53.8	62.7	47.2
M/v/v %	0	52.8	27.9	12.7	25.7	74.4	42.9
M/v/v %	5	62.9	30.4	41.2	71.8	80.5	53.3
M/v/v %	10	52.5	19.6	39.5	61.4	47.8	48.9

Experimental Design and Data Analysis. First, a four-factor, three-level factorial design was used to evaluate the effects of the following factors on the SFE efficiency: pressure (P) and temperature (T) of the supercritical fluid, dynamic extraction time (t), and volume of methanol added as the modifier (M). Nine experiments were performed in order to estimate the best conditions for the extraction of each cation. Factors and levels tested are reported in Table 1. Data obtained by performing experiments of the factorial design (Table 2) were analyzed by means of the Taguchi method[30] to calculate the main effects for each variable. (Table 3 shows the results of these computations.) The analysis of data when there is no interaction includes (1) determining the optimum condition, (2) identifying the individual influence of each factor, and (3) estimating the performance of the extraction at the optimum conditions.

Effect of Pressure and Temperature. Analyte solubility depends on a complex balance between supercritical fluid density and solute vapor pressure, both controlled by the temperature and pressure of the supercritical fluid. As can be inferred from the results, the pressure of the supercritical fluid plays an important role in the SFE of these cations from the solid matrix; in fact, it appeared to be significant for all of the analytes. This means that extraction recovery is usually enhanced as the pressure increases. The pressure increase causes an increase in the fluid density, and thus it could have a double effect: an increase in the solvating power of the supercritical fluid, responsible for quantitative recoveries, and reduced interaction between the fluid and the matrix as a consequence of the decreasing diffusion coefficient at higher density. As show in Table 4, for Bi^{3+}, Pd^{2+}, Mn^{2+}, and Ag^+ the best pressure for an efficient extraction is 300 atm, and for In^{3+} and Au^{3+}, the optimized pressure is 200 atm. Increasing temperature, although causing a decrease in the fluid density, could be responsible for an increase in the solvating power because of the increase in the solute vapor pressure. In this case, for In^{3+} and Ag^+ the best temperature for efficient extraction is 45 °C, and for the other metals (Pd^{2+}, Bi^{3+}, Mn^{2+}, and Au^{3+}), the temperature of the supercritical fluid was not found to be significant as the main effect; in fact, the temperature term does not appear in the yield estimate under optimized conditions for Pd^{2+}, Bi^{3+}, Mn^{2+}, and Au^{3+}.

Table 4. Optimum Condition for Extraction of Each Cation from the Solid Matrix

no.	cation	P/atm	T/K	t/min	M/v/v %
1	Ag^+	300	318		5
2	Pd^{2+}	300			
3	Mn^{2+}	300			
4	In^{3+}	200	318		5
5	Bi^{3+}	300			
6	Au^{3+}	200			

Table 5. Estimating the Extraction Efficiency at the Proposed Optimum Condition

no.	cation	% extraction	confidence interval
1	Ag^+	92	±7
2	Pd^{2+}	46	±11
3	Mn^{2+}	61	±15
4	In^{3+}	101	±4
5	Bi^{3+}	68	±12
6	Au^{3+}	72	±5

Effect of Dynamic Extraction Time. To achieve high recoveries, a first extraction step in static mode was performed; this step should make possible a better penetration of the fluid in the matrix than the dynamic mode. This step was followed by a dynamic extraction to enhance analyte solubility in the supercritical fluid.[32]

In the refined model, the main effect of dynamic extraction time does not have a significant effect on the efficiency of extraction of these metal ions. Therefore, to have a rapid extraction of these cations from the solid matrix, we can select a shorter extraction time (10 min).

Effect of Modifier. An essential drawback in the use of supercritical CO_2 is its low polarity, making the extraction of polar analytes difficult. Nevertheless, this limitation may be overcome by adding a small amount of polar modifiers, such as methanol or ethanol, to the supercritical CO_2 to increase its solvation power. Previous work indicates that methanol is the most effective modifier in the extraction of metal ions from a solid matrix.[33] Thus, it was chosen as the modifier in this study. The results of ANOVA showed that for Ag^+ and In^{3+} the presence of a modifier in the supercritical fluid is significant as the main effect. In the presence of 5% v/v methanol as the modifier, an increase in the extraction yield of these metals was observed, but the modifier has no main effect on the extraction efficiency of other cations (Pd^{2+}, Mn^{2+}, Au^{3+}, and Bi^{3+}). Furthermore, because analytes with different polarity show better recovery in the fluid added with methanol, the effect of the modifier is related not only to the change in polarity of the extraction fluid but also to its interaction with the matrix.

Projection of Optimum Performance. Recall that for a better quality characteristic the study of the main effect shows that the optimum conditions are shown in Table 5. As a general rule, the optimum performance will be calculated using the expression

$$Y_{\text{opt}} = \frac{T}{N} + \left(\bar{P}_x - \frac{T}{N}\right) + \left(\bar{T}_y - \frac{T}{N}\right) + \left(\bar{t}_z - \frac{T}{N}\right) + \left(\bar{M}_k - \frac{T}{N}\right)$$

Y_{opt} = average performance + contributions of P_x, T_y, t_z, and M_k above average performance where T is the grand total of all results, N is the total number of results, Y_{opt} is the performance under optimum conditions, and P_x, T_y, t_z, and M_k are the optimum pressure, temperature of the supercritical fluid, dynamic extraction time, and percentage of modifier volume, respectively.

The procedure for calculating the confidence interval of the optimum performance is discussed in the following text. The CI is given by

$$\text{CI} = \pm\sqrt{\frac{F_\alpha(f_1, f_2)\, V_\text{e}}{n_\text{e}}}$$

where $F_\alpha\,(f_1, f_2)$ = variance ratio for the degrees of freedom (DOF) f_1 and f_2 at the level of significance α (the confidence level is $(1 - \alpha)$); f_1 = DOF of mean (which always equals 1); f_2 = DOF of the error term; and n_e = number of equivalent replications, given by n_e = number of trials/DOF of the mean (always 1) + DOF of all resulting factors used in the estimate.

The results of determining the CI for the estimated value of the maximum extraction efficiency for the different metal cations are shown in Table 5.

Conclusions

The in situ chelation−SFE technique described in this paper provides a new method for extracting trace metal ions from solid samples. This sample preparation method avoids the use of acid leaching and organic solvent extraction required for the separation and concentration of trace metals using conventional methods. Metal ions such as Ag^+, Pd^{2+}, Mn^{2+}, In^{3+}, Au^{3+}, and Bi^{3+} adsorbed on filter paper can be effectively extracted by an in situ chelation−SFE technique using cyanex 301 as a chelation agent. The extraction efficiency of heavy-metal ions from the solid matrix with $SC-CO_2$ is influenced by a number of process parameters such as the pressure and temperature of the supercritical fluid, the dynamic extraction time, and the percentage of methanol volume used as a modifier.

As can be inferred from the results, the pressure of the supercritical fluid plays an important role in the SFE of these cations. For Ag^+ and In^{3+}, the temperature of the supercritical fluid was found to be significant as the main effect. Also, the results of ANOVA showed that the dynamic extraction time has no significant main effect on the extraction efficiency. However, for Ag^+ and In^{3+} the main effect of the modifier volumes is significant, and in the presence of 5% methanol as a modifier, the extraction efficiency increases.

The highest-percentage extractions of metal ions in the presence of cyanex 301 as a chelating agent with methanol-modified SC CO_2 using a factorial experiment design were also investigated. Finally, only the extraction of In^{3+} ions into SC CO_2 was found to be quantitative. Calculations showed that by using cyanex 301 as a ligand under the optimum extraction condition of SFE for each cation the extraction efficiencies will be 92 (±7)%, 46 (±11)%, 61 (±15)%, 101 (±4)%, 68 (±12)%, and 72 (±5)% for Ag^+, Pd^{2+}, Mn^{2+}, In^{3+}, Bi^{3+}, and Au^{3+}, respectively.

Supporting Information Available:

ANOVA data for each cation using the OA_9 (3^4) matrix and the extraction percent as the response. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Posting. This article was released ASAP on 8/4/2004. Changes were made to footnote a of Table 1 and references 2, 10, and 12. The paper was reposted on 8/27/2004.

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