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# Trace enrichment by solid-phase extraction for the analysis of heavy metals in water

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## Abstract

A combination of chelating heavy metals such as Ag(I), Cd(II), Cu(II), Ni(II) and Pb(II) with 4-(2-pyridylazo)resorcinol (PAR) and extraction on  $C_{18}$  cartridges prior to atomic absorption spectrometry was developed for trace metal analysis. Various factors, e.g., pH, PAR concentration, amount of  $C_{18}$  and flow-rate, were investigated in order to optimize the enrichment procedure. Water samples with an enrichment factor of 20 were analyzed. Results obtained gave a precision of 1–5%, and a recovery of 81–100%. The errors were in the range of 0.5–0.7% at the  $\mu\text{g/l}$  level.

## 1. Introduction

The determination of trace amounts of metals in water requires inevitably a concentration step prior to atomic absorption spectrometric (AAS) analysis. Conventional solvent extraction is mostly used for preconcentration, but it has many practical and technical limitations. Solid-phase extraction (SPE) has gained increased attention as a replacement for solvent extraction. The principles and methods of SPE have previously been published [1–6]. This technique is widely used [7,8]. Even though  $C_{18}$  SPE cartridges have been used previously for the separation of metal chelates, the application to the preconcentration of trace metals from aqueous solution is new. The complexation of the metal ions with 8-hydroxyquinoline followed by adsorption on  $C_{18}$  chemically bonded silica gel has been reported [9].

In the present paper, SPE has been developed

to analyze trace amounts of  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  in water. These metals formed metal–PAR chelates with 4-(2-pyridylazo)resorcinol (PAR) and their chelates can be trapped on a  $C_{18}$  SPE cartridge and then eluted with a suitable solvent. In this study, nitric acid is used as an eluent. The aim of these experiments is to study the effect of variables on the recovery of heavy metals. Several experimental variables have been evaluated: the eluent volume and concentration, the pH of the extracted solution, the flow-rate for the retention and elution steps, the concentration of PAR, and the sorbent mass. To achieve these objectives, Cd–PAR and Cu–PAR chelates were employed as models for this study. Suitable conditions were used for the determination of  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  as single components in water and then to determine the five metals as mixtures in water. In addition, the accuracy and precision of this technique were also studied.

## 2. Experimental

### 2.1. Reagents

For flash chromatography octadecyl bulk packing of 40  $\mu\text{m}$  average particle diameter (J.T. Baker, Phillipsburg, NJ, USA) was used without further purification. 4-(2-Pyridylazo)resorcinol (PAR) was purchased as the monosodium monohydrate salt (Merck, Darmstadt, Germany). Standard solutions for AAS (BDH) with concentrations of 1000 mg/l were used for the preparation of the working standard solutions and doubly distilled water was used throughout. All reagents were of analytical reagent grade.

The concentrations of the standard solutions of Cd and Cu used as models for this study were 0.05 mg/l and 0.02 mg/l, respectively.

### 2.2. Apparatus

The AAS measurements were carried out on a Shimadzu AA-670 (air-acetylene flame) instrument. Hollow-cathode lamps were employed as radiation sources. The operational conditions were those recommended by the manufacturer. A Baker-10 extraction system was used.

### 2.3. Procedure

Each  $\text{C}_{18}$  SPE cartridge for the evaluation of the variables was prepared by using a 4-ml polypropylene column. The steps for packing each cartridge were as follows: (1) put one piece of 10-mm glass fibre prefilter in a column, (2) pour 500 mg of octadecyl bulk packing into the cartridge, and (3) put another piece of 10-mm glass fibre prefilter over the packing.

Each cartridge must be activated before use by passing 3.0 ml of absolute methanol through the  $\text{C}_{18}$  SPE cartridge. To push the methanol downward, a vacuum pump must be used at 1333.22  $\text{N/m}^2$  pressure for ca. 30 s and then the pressure is decreased to 666.61  $\text{N/m}^2$ . After the absolute methanol reaches ca. 2 mm above the top of the packing, 2.0 ml deionized water is passed through the column.

A  $\text{C}_{18}$  SPE cartridge was equipped with a Baker-10 extraction system. A 100-ml metal-

PAR chelate solution was passed through the cartridge that had been activated before use. A vacuum pump was used to draw the solution down. For elution, dilute nitric acid was passed through the cartridge. The recovery of each metal under various conditions of sample preparation was calculated by comparing the sample absorbance of each metal with the standard solution. The results of the effect on the recovery are based on duplicate determinations.

The procedure for the precision study for each metal as a single component in water has been prepared by using the conditions that are summarized in Table 1. A series of solutions of each metal has been prepared for six determinations.

For the precision study of the five metals as mixtures in water the same conditions as for the study of the single components were used. Ten determinations were made for this study.

For the study of the accuracy a synthetic unknown mixture solution was used. Triplicate determinations were performed under the conditions mentioned earlier. The percent errors of each determination have been calculated on the assumption of 100% recovery of the metals (i.e., a concentration factor of 20) and has also been calculated using the recovery factor of each metal from the results of the precision study of the mixture components.

## 3. Results and discussion

### 3.1. The effect of nitric acid concentration

The results of the effect of nitric acid concentration on the recovery are presented in Table 2. The results show that the most suitable concentration of nitric acid is 1.0  $M$  for both metals. Therefore, this concentration is chosen as the optimal concentration for the study of each metal.

### 3.2. The effect of nitric acid volume

The results of the effect of the nitric acid volume on the recovery are presented in Table 3. The results show that the minimal volume of 1.0  $M$  nitric acid employed in this study to obtain the

Table 1  
Conditions for the determination of cadmium and copper as Cd-PAR and Cu-PAR chelates

Conditions	Cd	Cu	Conditions selected for both metals
HNO <sub>3</sub> conc.	1.0 M	1.0 M	1.0 M
HNO <sub>3</sub> volume	3.0 ml	4.0 ml	4.0 ml
pH of extraction	Increases in the basic solution	Decreases in the basic solution	7–8
Flow-rate in the retention step	3.0 ml/min	6.0 ml/min	6.0 ml/min
Flow-rate in the retention step	0.1 ml/min	0.5 ml/min	6.0 ml/min
Excess of PAR concentration over metal	50 fold	20 fold	50 fold
Sorbent mass	50 mg	400 mg	500 mg

maximal percentage recovery is 4.0 ml for cadmium and 3.0 ml for copper. Hence, 4.0 ml of nitric acid is chosen as the optimal volume for the study of each metal.

### 3.3. The effect of pH

The results of the effect of the pH of the extracted solution on the recovery are presented in Table 4. The results show that the recovery of cadmium increases in the basic solution (above pH 8.0) while the recovery of copper decreases in the basic solution. The pH of the extracted

solution should be ca. 7.0–8.0 to prevent the formation and precipitation of metal-hydroxide complexes in basic solution, which causes loss of analyte species.

### 3.4. The effect of flow-rate in the retention step

The results of the effect of the flow-rate in the retention step on the recovery are presented in Table 5. The results show that the optimal flow-rate obtained is 3.0 ml/min for cadmium and 6.0 ml/min for copper. To reduce the analysis times,

Table 2  
Effect of nitric acid concentration on the recovery by using Cd-PAR and Cu-PAR chelates as models

Element	Conc. of HNO <sub>3</sub> (M)	Recovery (%)
Cd	0.1	63.80
	0.5	73.50
	1.0	75.80
	2.0	62.20
	4.0	60.30
Cu	0.1	94.50
	0.5	101.50
	1.0	102.75
	2.0	102.50
	4.0	101.10

Table 3  
Effect of volume of nitric acid solution on the recovery by using Cd-PAR and Cu-PAR chelates as models

Element	Volume of 1.0 M HNO <sub>3</sub> (ml)	Recovery (%)
Cd	1.0	68.10
	2.0	70.30
	3.0	71.60
	4.0	74.20
	5.0	73.80
Cu	1.0	87.25
	2.0	96.75
	3.0	99.75
	4.0	99.75
	5.0	99.75

Table 4  
Effect of pH of extracted solution on the recovery by using Cd-PAR and Cu-PAR chelates as models

Element	pH of extracted solution	Recovery (%)
Cd	5.0	69.60
	6.0	74.70
	7.0	73.90
	8.0	81.20
	9.0	85.20
	10.0	87.70
Cu	1.0	101.00
	2.0	102.75
	3.0	100.51
	4.0	101.00
	5.0	94.75
	10.0	51.00

the fastest flow-rate is the best choice to select. By using the instrument in this laboratory, a flow-rate of 6.0 ml/min is chosen for the study of each metal; higher flow-rates cannot be used due to the overload of the motor.

### 3.5. The effect of flow-rate in the elution step

The results of the effect of the flow-rate in the elution step on the recovery are presented in

Table 5  
Effect of flow-rate in the retention step on the recovery by using Cd-PAR and Cu-PAR chelates as models

Element	Flow-rate in retention step (ml/min)	Recovery (%)
Cd	2.0	78.60
	3.0	80.40
	4.0	76.20
	6.0	78.70
	8.0	78.60
	10.0	78.00
Cu	2.0	97.75
	3.0	98.25
	4.0	99.00
	6.0	100.50
	8.0	99.00
	10.0	99.25

Table 6  
Effect of flow-rate in the elution step on the recovery by using Cd-PAR and Cu-PAR chelates as models

Element	Flow-rate in elution step (ml/min)	Recovery (%)
Cd	0.1	80.90
	0.5	78.00
	1.5	80.50
	3.0	76.00
	6.0	74.50
	9.0	73.10
Cu	0.1	94.25
	0.5	96.50
	1.5	91.25
	3.0	93.00
	6.0	92.25
	9.0	90.25

Table 6. The results show that the optimal flow-rate in this study is 0.1 ml/min for cadmium and 0.5 ml/min for copper. When the flow-rate changes to higher values, the recovery does not change significantly. In order to reduce the analysis times, a flow-rate of 6.0 ml/min is chosen for the study of each metal.

### 3.6. The effect of PAR concentration

The results of the effect of the PAR concentration on the recovery are presented in Table 7. The results show that the concentration of PAR at 50-fold excess over concentration of cadmium and 20-fold excess over concentration of copper are preferred. For the analysis of these metals as mixtures in water, the large excess of PAR concentration (over 50-fold) is recommended.

### 3.7. The effect of sorbent mass

The results of the effect of sorbent mass on the recovery are presented in Table 8. The results show that the minimal sorbent mass obtained from this study is 500 mg for cadmium and 400

Table 7  
Effect of concentration of PAR on the recovery by using Cd–PAR and Cu–PAR chelates as models

Element	Conc. of PAR excess over conc. of metal (fold)	Recovery (%)
Cd	5	76.30
	10	77.90
	20	77.10
	50	82.80
	100	81.20
Cu	5	99.55
	10	98.75
	20	104.00
	50	100.25
	100	99.75

Table 8  
Effect of sorbent mass on the recovery by using Cd–PAR and Cu–PAR chelates as models

Element	C <sub>18</sub> SPE mass (mg)	Recovery (%)
Cd	100	33.70
	200	48.50
	300	67.30
	400	80.40
	500	82.80
Cu	100	76.00
	200	96.50
	300	97.75
	400	102.00
	500	98.75

Table 9  
Precision for the determination of each metal as single components in water on a C<sub>18</sub> SPE cartridge

Metal	mg/l	Detection limit (mg/l)	Average recovery <sup>a</sup> (%)	Relative standard deviation (%)
Ag	0.05	0.06	81.82	3.11
Cd	0.05	0.03	84.81	3.47
Cu	0.02	0.09	96.08	1.53
Ni	0.20	0.05	95.36	1.48
Pb	0.05	0.30	81.64	1.01

<sup>a</sup> The average recovery for these metals were obtained from six determinations.

mg for copper. Hence, the sorbent mass at 500 mg is chosen as the optimal mass for the study of each metal.

The suitable conditions for determination each metal can be performed by using the selected conditions that are summarised in Table 1.

The results of the precision on C<sub>18</sub> SPE cartridges for determining each metal as a single component in water are shown in Table 9. The average recoveries and the relative standard deviations for Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> are 81.82 ± 3.11, 84.81 ± 3.47, 96.08 ± 1.53, 95.36 ± 1.48 and 81.64 ± 1.01%, respectively. The average recoveries with relative standard deviations for these metals as mixture components in water for Ag<sup>+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> are 81.05 ± 4.97, 89.41 ± 3.88, 100.86 ± 1.15, 98.62 ± 1.93 and 83.57 ± 4.35%, respectively for *n* = 10. This technique can be used as an efficient sample preparation procedure for the determination of each metal as a single component in water or as mixtures of metals in water. Recoveries of these metals in both cases show insignificant differences.

The accuracy of this technique was also evaluated by the determination of a mixture of metals in an unknown synthetic solution and the results are shown in Table 10. The errors of Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> are 15.98, 4.34, 0.29, 5.0 and 13.40% (by using the assumption of 100% recovery). The large value of the errors can be reduced by taking into account the recovery factors of these metals. Then the errors of Ag<sup>+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> are 3.64, 6.98, 0.59, 3.69 and 3.63%, respectively. It is indicated that

Table 10  
Precision for the determination each metal as mixture components in water on a C<sub>18</sub> SPE cartridge

Metal	1	2	3	4	5	6	7	8	9	10	Average recovery (%)	Relative standard deviation (%)	
Ag	Absorbance	0.163	0.174	0.183	0.172	0.168	0.175	0.161	0.157	0.161	0.163	0.163	
	Concentration Recovery (%)	1.572	1.683	1.770	1.666	1.626	1.695	1.552	1.516	1.552	1.578	1.578	4.97
Cd	Absorbance	0.142	0.144	0.149	0.140	0.146	0.138	0.132	0.142	0.143	0.137	0.137	
	Concentration Recovery (%)	0.897	0.912	0.949	0.884	0.929	0.868	0.827	0.899	0.909	0.867	0.867	3.88
Cu	Absorbance	0.235	0.235	0.232	0.233	0.232	0.229	0.237	0.236	0.232	0.232	0.232	
	Concentration Recovery (%)	4.061	4.075	4.006	4.027	4.014	3.945	4.103	4.083	4.019	4.012	4.012	1.15
Ni	Absorbance	0.212	0.223	0.215	0.211	0.215	0.209	0.211	0.213	0.215	0.211	0.211	
	Concentration Recovery (%)	3.914	4.126	3.978	3.892	3.985	3.859	3.897	3.930	3.973	3.896	3.896	1.93
Pb	Absorbance	0.229	0.240	0.230	0.220	0.234	0.234	0.230	0.241	0.234	0.232	0.232	
	Concentration Recovery (%)	8.041	8.514	8.078	7.666	8.250	8.848	8.362	8.821	8.548	8.441	8.441	4.35
		80.41	85.14	80.78	76.66	82.50	88.48	83.62	88.21	85.48	84.41	83.57	4.35

this technique is suitable for determining of trace levels of these metals with good results.

#### 4. Conclusion

An efficient sample preparation method using solid-phase extraction for enhancing the concentration of some heavy metals in water was developed. High percent recoveries are obtained because there is no formation of emulsion, only a small amount of sample transfer, and using small volumes of extraction solvent results in little or no evaporation. It is also a simple, rapid, economical and safe method.

For future work, larger extraction volumes should be studied in order to give a better enrichment factor of the metals in the final volume. The design of a new apparatus can be improved by increasing the flow-rate of solutions studied. The detection limit and sensitivity of other metals can be determined by using this sample preparation technique with other instru-

ments, i.e., graphite furnace or inductively-coupled plasma atomic absorption spectroscopy. Other ligands are also interesting to study for improving sensitivity and selectivity. The investigation of other heavy metals in water and various environmental samples should be also considered.

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