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SHORT COMMUNICATION

GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF CADMIUM AFTER SOLID-LIQUID EXTRACTION WITH DITHIZONE

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ABSTRACT. A method for the determination of trace amount of cadmium ion after preconcentration by extracting its dithizone complex into molten naphthalene was developed. Several experimental conditions such as pH of the solution, stirring time, the amounts of naphthalene, standing time and volume of the solution were optimized. Trace amount of cadmium ion in aqueous solution of sample was chelated with 5 mL of 0.001 M dithizone at pH 8. After addition of 0.15 g naphthalene, the solution was heated to about 85 ^{o}C and stirred (800 rpm) for 2 min to reproduce the microcrystalline naphthalene. Cadmium ion was determined by a graphite furnace atomic absorption spectrometer. The interfering effects of diverse concomitant ions (cations and anions) were investigated. Artificial sea water and a standard reference material (SRM) were analyzed by this method. The sensitivity and detection limit of 1.2 ngL^{-1} and 1.5 ng L^{-1} were found, respectively.

KEY WORDS: Cadmium, Dithizone, Preconcentration, Atomic Absorption Spectrometry

INTRODUCTION

From an analytical standpoint, the selection of the appropriate method is not always a facile-undertaking since it depends on many factors related to the available detection device, the required detection limits, the reproducibility and recovery of the method as well as the potential interferences stemming from the sample matrix composition. As a result of the synergistic effect of all these factors a compromise should be pursued when multi-analyte determinations are of concern [1]. Although highly sophisticated techniques like ICP offer the necessary versatility to resolve most of these issues [2], their application to monitoring surveys is rather limited by the high operational and maintenance cost involved with their use, especially when a large number of samples must be analyzed. Therefore, the provision of analytical protocols that combines optimum analytical features with low analysis cost is a continuous challenge for the analytical community [3-5].

Solvent extraction is one of the most widely used techniques owing to its simplicity and applicability to both trace and macro amounts of metal ions. However, the method is limited in its applicability because of the mutual solubility of the two phases and possible formation of an emulsion on shaking.

Typically, solid phase extraction replaces liquid-liquid extraction as a sample preconcentration tool and provides a method that is simple and safe to use [6]. In recent years, the solid phase extraction cartridges and columns have been successfully used for the separation and sensitive determination of metal ions, e.g., preconcentration of uranium(IV) with microcrystalline naphthalene [7], extraction of uranium(IV) with ocadecylsilica membrane [8], preconcentration of indium on microcrystalline naphthalene [9], separation of manganese with 2-(5-boromo-2-pyridylazo)-5-diethylamino phenol [10], and determination of antimony after preconcentration with 2-nitroso-1-naphtalo-4-sulphonic acid [11]. At the high temperatures the

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water-insoluble complex is extracted into the molten solid solvent to achieve distribution equilibrium. After the equilibration, the phase separation can be obtained by cooling the extraction system to room temperature.

As a powerful chelating agent, dithizone can react with the majority of metal ions in the periodic table to form colored chelate complexes. Therefore, this reagent has been applied widely to liquid-liquid extraction separation in analytical chemistry [12-15].

In the present work, we have developed a simple, rapid, sensitive and economical method for the direct AAS determination of cadmium after its preconcentration by extracting its dithizone complex into molten naphthalene.

EXPERIMENTAL

Instrumentation. A Shimadzu (model AA-670G, Japan) atomic absorption spectrometer with a GFA-4B graphite furnace atomizer with deuterium lamp background correction was used. Methrom pH meter (model 691, Switzerland) with a combined glass and calomel electrode was used to adjust the pH of the test solutions.

Reagents. All chemicals used were of analytical or guaranteed-grade reagents and purchased from Merck, Germany. The deionized water was used throughout the experiments. Cadmium nitrate standard solution (10 mgL^{-1}) was made from cadmium stock solution (1000 mgL^{-1}). The dithizone solutions (0.001 M) were made in acetone. The interfering solutions were made from stock solutions (1000 mgL^{-1}) or by dissolving their salts in water and diluting appropriately.

Procedure. A 10 mL sample solution was pipetted into a 100 mL Erlenmeyer flask, and 5 mL 0.00l M dithizone was added as a complexing agent. The pH was adjusted to 8 (optimum value) with 0.001 M NaOH or 0.001 M HCl. The aqueous phase was diluted to 40 mL. The amount of 0.15 g naphthalene was added as a solid solvent. Then, this solution was heated in a water bath to about 85 ^{o}C and stirred (800 rpm) for 2 min to dissolve the complex in the molten naphthalene, and allowed to stand for 15 min at room temperature to form micro crystalline naphthalene containing Cd-dithizone complex. After filtration with fritted glass, this microcrystalline naphthalene was washed with deionized water and dissolved in a 2 mL volumetric flask with acetone. The absorbance of the solutions was measured at 228.8 nm with graphite furnace atomic absorption spectrometer. A calibration curve was prepared in the range 0-40 ngmL^{-1} of cadmium according to the general procedure. The amount of cadmium in the sea water and SRM (reference samples) were measured according to the general procedure.

RESULTS AND DISCUSSION

The values of the experimental parameters such as pH of sample solution, amount of naphthalene, standing time, stirring rate and effect of volume of aqueous phase were optimized. The optimum values of the parameters were found in separate experiments.

Effect of pH. The pH of 30 mL solution containing 10 mgL^{-1} of cadmium and 5 mmol dithizone was carefully adjusted from 4 to 9 with 0.001 M HCl or 0.001 M NaOH to form the Cd-dithizone complex quantitatively. Table 1 shows the variation of absorbance of the complex against pH of the solution. As it is shown in Table 1, the absorbance of cadmium ion extracted, is dependent on the pH and the maximum absorbance was observed in the range of pH 7-9. A pH 8 was chosen for the measurements.

Table 1. Effect of experimental parameters on the extraction of cadmium ions.

pH	Abs.	Amount of Naphthalene (g)	Abs.	Standing time (min)	Abs.	Stirring rate (rpm)	Abs.	Aqueous phase (mL)	Abs.
5	0.080	0.02	0.135	2	0.100	0	0.080	5	0.120
6	0.120	0.04	0.140	5	0.130	200	0.110	10	0.132
6.5	0.170	0.06	0.145	10	0.140	400	0.130	15	0.152
7	0.200	0.08	0.150	15	0.220	600	0.160	20	0.170
7.4	0.220	0.10	0.170	20	0.224	800	0.190	25	0.180
7.8	0.230	0.12	0.190	25	0.226	1000	0.192	30	0.185
8.2	0.225	0.14	0.192			1200	0.191	35	0.190
8.6	0.215	0.16	0.193					40	0.192
9	0.200							45	0.194

Amount of naphthalene. The amount of naphthalene was varied from 0.02 to 0.16 g in order to investigate the efficiency of Cd-dithizone complex that was extracted into the molten naphthalene. Table 1 shows the results of effect of naphthalene to the absorbance of Cd-ditizone complex. The complex was quantitatively extracted after the addition of more than 0.1 g naphthalene. As it is shown in Table 1, for the amount less than 0.12 g, the extraction was incomplete.

Effect of stirring rate. The stirring rate affects the distribution of complex dissolved in the solid phase at 85 ^{o}C. The stirring rate was controlled between 0 to 1200 rpm. Table 1 shows the effect of stirring rate on the Cd-dithizone absorbance. As it is shown in Table 1, there is no difference between the absorbances of extracted Cd(II) ions for stirring rates higher than 800 rpm. Thus, 800 rpm stirring rate was used in the standard measurements.

Effect of standing time. The effect of standing time of the complex in microcrystalline naphthalene after its extraction at 85 ^{o}C from the aqueous solution of sample was studied. The extract (Cd(II)-dithizone complex in naphthalene was allowed to stands at room temperature from 2 to 25 min (Table 1). The absorbance of cadmium complex was remained constant after 15 min. The absorbance of the Cd-dithizone complex in naphthalene-acetone solution was constant for more than 24 h. A standing time of 15 min was used before the separation.

Effect of volume of the aqueous phase. The volume of the aqueous phase was varied from 5 to 60 mL with the constant concentration of cadmium ions. The absorbance was remained constant up to 40 mL of the volume of aqueous solution. Table 1 shows the effect of volume of the aqueous phase on the absorbance of cadmium complex. As it is shown in Table 1, above 40 mL of the aqueous phase solution, there is no change in the absorbance.

The calibration curve and effect of foreign ions. To obtain the calibration curve, after preparation the standard solutions of Cd^{2+}, analysis of the solutions were done (n = 5) as described in the general procedure under the optimum conditions. The calibration curve corresponds with the range from 0 to 40 $ngmL^{-1}$ of cadmium. The correlation coefficient, r, was found to be 0.9986 for the calibration curve. In the present method, detection limit is found based on three times the standard deviation of blank. Also, the sensitivity of the method was found from the slope of the calibration curve. The detection limit and sensitivity of the method were found 1.2 ngL^{-1} and 1.5 ngL^{-1}, respectively.

It was necessary to investigate the effect of concomitant ions on the determination of cadmium according to this method. The results of interference studies and the conditions of the experiments are shown in Table 2. As it is shown in Table 2, most of the ions have no interfering effect under the mentioned conditions. Mercuric, zinc(II), cobalt(II) and silver(I) ions have the positive interference effect on the absorbance of cadmium. While, germanium(IV), copper(II), lead(II) and antimaony(III), have the negative interference effect on the absorbance of cadmium in the same conditions. Table 3, shows the results of determination of cadmium in SRM and artificial sea water.

Table 2. The effect of interference ions on determination of 10 ngmL^{-1} cadmium in the presence of 100 fold of foreign ions.

Ion	Relative absorbance[a,*]	Ion	Relative absorbance
Ag(I)	1.2	Pb(II)	0.94
Al(III)	1.00	Sb(III)	0.95
Ba(II)	1.00	Se(IV)	1.00
Bi(III)	1.00	Sn(II)	1.00
Ca(II)	1.00	Sr(II)	1.00
Co(III)	1.20	Br^-	1.00
Cu(II)	0.98	Cl^-	1.00
Fe(III)	1.00	I^-	1.00
Ge(IV)	0.94	F^-	1.12
Hg	1.3	NO_3^-	1.00
Mg(II)	1.00	PO_4^{3-}	1.00
Na(I)	1.00	SO_4^{2-}	1.00
Zn(II)	1.2		

[*]The results are the average of triplicate measurements. [a]The relative absorbance is defined as:

$$\text{Relative absorbance} = \frac{(\text{Absorbance of 10 ng mL}^{-1}\text{ cadmium + foreign ion 1 }\mu\text{g mL}^{-1})}{\text{Absorbance of 10 ng mL}^{-1}\text{ cadmium}}$$

Table 3. Results (mean ± standard deviation based on five replicate analysis) of determination of cadmium in SRM and artificial sea water.

Sample	Cadmium added (ng mL^{-1})	Cadmium found (ng mL^{-1})	Recovery %
Artificial sea water[a]	0	5.2 ± 0.3	_
	5	9.7 ± 0.58	95
	10	14.7 ± 0.88	97
	15	20.6 ± 1.23	102

SRM	Reported value	Measured value	Recovery %
JR-1[b]	0 .026 (μg g^{-1})	0.027 ± 0.016 (μg g^{-1})	104
JG-1a[b]	0.026 (μg g^{-1})	0.027 ± 0.0016 (μg.g^{-1})	105

[a]Composition of artificial sea water: NaCl, 0.4266 mol kg^{-1}; Na_2SO_4, 0.0292 mol kg^{-1}; KCl, 0.0105 mol kg^{-1}; $CaCl_2$, 0.0107 mol kg^{-1}; $MgCl_2$, 0.0551 mol kg^{-1}. [b]obtained from geological survey of Japan, GSJ.

CONCLUSIONS

We have introduced naphthalene as a new and cheap solid solvent for the extraction of cadmium ions from the aqueous phase. It has several advantages such as simplicity, high recovery and sensitivity. The LOD and sensitivity of the method is comparable or in some cases better than some of the previously reported preconcentration methods [16-18]. The investigated procedure was successfully applied for the analysis of artificial sea water and standard reference material.

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