Determination of Cadmium and Zinc in Fertilizer Samples by FAAS after Solid-Phase Extraction with Freshly Precipitated Manganese-diethyldithiocarbamate

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Using freshly precipitated manganese-diethyldithiocarbamate (Mn(DDTC)_2) as a new reagent, a solid phase extraction method (SPE) has been developed for the extraction of Cd(II) and Zn(II) in aqueous fertilizer samples. A sample solution of 300 mL was taken and 0.10 g of freshly precipitated Mn(DDTC)_2 was added. After adding a phosphate buffer solution, the mixture was stirred at 10 min, filtered with a glass filter and washed with deionized water. The solid product containing Mn(DDTC)_2 -Cd(DDTC)₂-Zn(DDTC)₂ complexes was dissolved in concentrated nitric acid and its volume was made complete up to 10 mL with deionized water. The metal contents of the solution were measured by an atomic-absorption spectrometer.

(Received November 11, 2005; Accepted January 30, 2006)

Flame atomic-absorption spectrometry (FAAS) is one of the most popular techniques for the determination of trace metals in industrial fertilizers or some environmental samples, due to being useful, inexpensive and selective. However, for extremely low analyte concentrations and matrix effects (such as PO_4^{3-} , Cl^- and SO_4^{2-} ions) a preliminary preconcentration or separation technique is required.

The solid phase extraction method (SPE) is generally used for the preconcentration of metal ions in various matrices.¹⁻⁶ In this technique, the dithiocarbamate extraction method is a useful means of enrichment, and dithiocarbamates do not react with many metals that are fairly abundant in environmental samples. To the preconcentration of trace metals, it has been applied prior to their determination by UV-VIS spectrophotometry,⁷⁻¹⁵ AAS,¹⁶⁻²¹ ICP-AES^{22,23} and electroanalytical method.^{24,25}

In these studies, sodium diethyldithiocarbamate (NaDDTC), ammonium pyrolidinedithiocarbamate (APDC) or ammonium hexamethylenedithiocarbamate (HMDC) reagent was added to an aqueous phase containing several metals. Then, metal-dithiocarbamate complexes were formed and all of them were extracted on a solid phase, such as activated carbon, polyurethane foam, silica gel or amberlite XAD resins. In these applications, there were some difficulties, such as dithiocarbamate anions that decomposed in aqueous acidic medium. The selective extraction of the metal ions could not be achieved.

On the other hand, several dithiocarbamate reagents have been used prior to an atomic-absorption spectrometric determination for the preconcentration of trace metals, as a coprecipitant with a carrier element, such as Ni(II)²⁶ and Bi(III).²⁷ In this method, the selective extraction of the metal ions is not possible because some ions in solution simultaneously precipitate when the precipitation occurs with a carrier element.

In our preceding work, freshly precipitated metal diethyldithiocarbamates (Mn(DDTC)_2 , Zn(DDTC)_2 ,

Cd(DDTC)_2 , Fe(DDTC)_3 , Co(DDTC)_2 , Cu(DDTC)_2 , Ni(DDTC)_2 , Pb(DDTC)_2 and Hg(DDTC)_2) were tested as reagents for the selective extraction of Mn(II), Zn(II), Cd(II), Fe(III), Co(II), Cu(II), Ni(II), Pb(II) and Hg(II) ions from aqueous solution. It was found that these reagents show excellent selectivity for the extraction of metal ions.²⁸

In this present study, a new application of these reagents was carried out, where freshly precipitated Mn(DDTC)_2 was used for the preconcentration of Cd and Zn in an aqueous system prior to their determination by FAAS. The aim of this work was to investigate the optimum conditions for the selective extraction and atomic-absorption spectrophotometric determination of Cd and Zn in some fertilizer samples.

Experimental

Apparatus and reagents

An ATI-UNICAM 929 Model flame atomic-absorption spectrophotometer was used for the determination of metal ions. pH measurements were performed with a JENWAY 3040 Model digital pH-meter. C, H, N and S analyses were carried out by CHNS-932 (LECO) at the TUBITAK ATAL Research Centre (Ankara). Sodium salt of diethyldithiocarbamic acid was purchased from E. Merck. Cd(II) and Zn(II) stock solutions (0.1 mol L^{-1}) were prepared by dissolving appropriate amounts of their nitrate salts. Standard solutions for AAS were prepared with the stock metal solutions. Deionized water was produced by ELGA Maxima Ultra Pure Water Systems. Other reagents were of analytical reagent grade.

Preparation of Mn(DDTC)_2 precipitate

A Mn(II) solution in water (0.1 mol L^{-1}) and a NaDDTC solution (0.1 mol L^{-1}) in water were mixed in stoichiometric ratio, and Mn(DDTC)_2 was precipitated. The precipitant was filtered with filter paper by a vacuum pump. It was washed with deionized water and stored in a flask while being

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Fig. 1 Effect of the pH for the preconcentration of cadmium and zinc.

Fig. 2 Effect of the aqueous phase volume on the preconcentration of cadmium and zinc.

somewhat damp. If the metal dithiocarbamate was dried, it became fixed in the water solution during the extraction procedure, and was not completely mixed with the aqueous phase.

Mn(DDTC)₂ was dried at 110°C for 24 h. The humidity was found to be 30.2%. Dried Mn(DDTC)₂ was characterized by elemental analysis. The calculated and found (in parentheses) C, H, N and S were 34.20 (34.18), 5.70 (5.14), 7.97 (7.76) and 36.47 (36.91).

General procedure

A solution of 300 mL, containing 30–200 µg Cd(II) and Zn, was placed in an Erlenmeyer flask, and 0.10 g of freshly precipitated Mn(DDTC)₂ was added. After adding the phosphate buffer solution, the mixture was stirred at 10 min, filtered with a glass filter and washed with deionized water. The solid product containing Mn(DDTC)₂-Cd(DDTC)₂-Zn(DDTC)₂ complexes was dissolved in concentrated nitric acid and its volume was made up 10 mL with deionized water. The metal contents of the solution were measured by an atomic-absorption spectrophotometer.

Results and Discussion

Effect of the pH

The SPE productivity depends on various parameters. The pH is one of the most important parameters, and first of all pH must be determined. For this purpose, 50 mL of solutions containing 5 µg of a cadmium and zinc solution were taken, and the pH was adjusted by HNO₃ and KOH solutions. The other parameters being constant, the general procedure was applied and the concentrations of metals were measured by FAAS. The results presented in Fig. 1 indicate that the extraction of

Fig. 3 Effect of extraction period for the preconcentration of cadmium and zinc.

cadmium and zinc on solid Mn(DDTC)₂ has no effect between pH 4–7.

The stability of metal-DDTC depends on the pH. A higher stability constant of metal-DDTC means more stable in acidic solutions; also, sorption can be carried out at low pH degrees. The stability constant of Cd(DDTC)₂ is greater than that of Zn(DDTC)₂, and Cd(II) can be extracted in a more acidic solution.

Effect of the aqueous phase volume

The volume of the aqueous phase is an important factor for the extraction of metal ions. To determine the effect of the volume of the aqueous phase, cadmium and zinc solutions (containing 5 µg mL⁻¹ of Cd(II) and Zn(II)) were diluted from 50 to 500 mL by deionized water, and the metal content was analyzed by the general procedure. The results are presented in Fig. 2. It was shown that the cadmium and zinc concentrations remained constant up to 500 mL. It is indicated that the exchange reaction of metals is rapid, and the efficiency is high. The aqueous phase volume was selected to be 300 mL for confidence. The enrichment factor achieved for the proposed method was 30.

Effect of the extraction period

The extraction period was also studied; cadmium and zinc solutions (containing 5 µg mL⁻¹ of Cd(II) and Zn(II)) extracted at various periods according to previously described procedure and the absorbance of metals measured by FAAS. The results are presented in Fig. 3. It was observed that the quantitative extraction of Cd and Zn was completed at 5 min. The extraction time was selected to be 10 min for confidence.

Effect of diverse ions

Chemical fertilizers generally consist of alkali metal ions (or NH₄⁺) and anions such as nitrate, chloride, phosphate or sulfate. Therefore, to investigate an interfering effect of the diverse ions, saturated salt solutions were used. A metal solution (containing 5 µg mL⁻¹ of Cd(II) and Zn(II)) and different amounts alkali metal salt solutions were prepared. The determinations of cadmium and zinc contents were carried out by the general procedure. The results given in Table 1 indicated that many of the salts and metal ions can be tolerated up to saturated levels.

Sorption capacity of the solid Mn(DDTC)₂

The freshly precipitated Mn(DDTC)₂ solid-phase sorption

Table 1 Effect of diverse salts on the determination of cadmium and zinc

Salt	Tolerance limit ^a for Cd/g L ⁻¹	Tolerance limit ^a for Zn/g L ⁻¹
KCl	140	140
Na ₂ SO ₄	70.6	70.6
KNO ₃	120	120
(NH ₄) ₃ PO ₄	60	60
KBr	120	120
NaAc	60.2	60.2
(NH ₄) ₂ SO ₄	200	200
NaCl	160	160

a. Tolerance limit was taken as the amount causing an error of $\pm 5\%$ in absorbance.

Table 2 Linear ranges, calibration equations, limit of detections and limit of quantifications

	Linearity	Equation	R ²	LOD	LOQ
Cd	0.2 – 3	$y = 0.118x + 0.025$	0.983	0.04	0.08
Zn	0.2 – 4	$y = 0.134x + 0.014$	0.993	0.25	0.49

capacity was studied. A metal solution of 100 mL (0.1 mol L⁻¹) was taken and 0.1 g of freshly precipitated Mn(DDTC)₂ was added. To adjusted the pH of the solution, a phosphate buffer solution was added. The procedure was applied and the metal contents were measured by AAS. The results demonstrated that 1.00 g of freshly precipitated Mn(DDTC)₂ had a capacity of 199 mg of Cd(II) and 116 mg of Zn(II).

The sorption of the metal ions was carried out by exchanging Mn(II) and Cd(II)_(aq) or Zn(II)_(aq) species on freshly precipitated Mn(DDTC)₂;

The stability of metal-DDTC's decreases in the following order: Hg, Cu, Pb, Ni, Cd, Fe, Co, Zn and Mn. The element can be displaced from its diethyldithiocarbamate compound only by elements to the left of it in the series.²⁸ However, the sorption capacity depends on several parameters, such as the stability constant of metal DDTC's, the pH and kinetics factors.

Calibration curve, linearity and sensitivity

The calibration graph was constructed with ten standard solutions containing 0.1–20 µg mL⁻¹ of cadmium or zinc according to the general procedure. The range of linearity was determined to be 0.2–3 µg mL⁻¹ for cadmium and 0.2–4 µg mL⁻¹ for zinc. The linearly ranges, regression equation and correlation coefficient were obtained by the method of least squares. The limit of detection and the limit of quantification were evaluated as the concentration corresponding to three times and ten-times the standard deviation of the blank signal, respectively. The results are presented in Table 2.

Determination of Cd and Zn in fertilizer samples

The proposed method was successfully applied to the determination of Cd(II), and Zn(II) in chemical fertilizer samples. Fertilizer samples were taken from TUGSAŞ (Türkiye Gübre Fabrikaları Sanayi Anonim Şirketi). The samples were dissolved in a nitric acid solution (1%) and filtered. Freshly precipitated Mn(DDTC)₂ (0.1 g) was added. Their pH were

Table 3 Determination of Cd and Zn in fertilizer samples

Fertilizer sample	Cd/µg kg ^{-1a}	Zn/µg kg ^{-1a}
UREA	LOQ	204 ± 20
KNO ₃	LOQ	330 ± 30
NH ₄ NO ₃	17.2 ± 1.4	200 ± 17
(NH ₄) ₂ SO ₄	7.1 ± 1.5	222 ± 39

a. Mean of three determinations with 95% confidence level ($\bar{X} \pm ts/\sqrt{N}$).

Table 4 Determination of Cd and Zn in spiked fertilizer samples

Fertilizer sample	Spiked Cd and Zn/µg ⁻¹	Found ^a	
		Cd/µg ⁻¹	Zn/µg ⁻¹
UREA	1.00	0.92 ± 0.03	0.91 ± 0.01
KNO ₃	1.00	0.89 ± 0.02	0.89 ± 0.05
NH ₄ NO ₃	1.00	0.79 ± 0.16	0.90 ± 0.02
(NH ₄) ₂ SO ₄	1.00	0.98 ± 0.05	0.94 ± 0.06

a. Mean of three determinations with 95% confidence level ($\bar{X} \pm ts/\sqrt{N}$).

Table 5 Determination of Cd and Zn in certified reference

BCR 32 Moroccan phosphate rock	Certified value/µg ⁻¹	Found ^a /µg ⁻¹
Cd	20.8	20.3 ± 2.0
Zn	253	248 ± 15

a. Mean of three determinations with 95% confidence level ($\bar{X} \pm ts/\sqrt{N}$).

adjusted by a phosphate buffer and analyzed by the procedure. The results are presented in Table 3.

Accuracy check of the method

For an accuracy check of the method, a certified reference material (CRM, BCR-32 Moroccan phosphate rock) and metal spiked (Cd and Zn) fertilizer samples were used. An aliquot of the solution of the certified material was taken and the metal contents were determined by the proposed method. The recovery values calculated for the standard additions were between 79–98% and for the certified reference material were 97–98%. The results given in Tables 4 and 5 indicate that the certified and found values are very concordant.

Conclusion

SPE is currently popular and more advantageous than other techniques for the preconcentration of trace metal ions prior to their determination by AAS due to being rapid and simple, and allowing preconcentration from a larger volume of samples. The reactivity is very important in this technique, and dithiocarbamates do not react with many metals (such as IA and IIA groups metals), which are fairly abundant in fertilizer samples. Thus, selectivity can be achieved by using freshly precipitated manganese diethyldithiocarbamate in the solid-phase extraction procedure. This method is based on the fact that the stability constants of the Cd and Zn dithiocarbamate complexes are greater than that of the Mn(DDTC)₂ complex. Therefore, the metal ions in water rapidly exchange for Mn(II) on the Mn(DDTC)₂ solid phase. The solid phase can be easily

dissolved in nitric acid, and its absorbance can be measured by FAAS. Consequently, the proposed method is simple, selective, sensitive and accurate. It can be used for the determination of cadmium and zinc in fertilizer samples and other like samples.

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