

# Determination of Cadmium by FAAS After Solid-Phase Extraction of its 1-Benzylpiperazinedithiocarbamate Complex on Microcrystalline Naphthalene

Hasan CESUR, Bekir BATI

*Department of Chemistry, Faculty of Art and Science, Ondokuz Mayıs University,  
TR-55139 Samsun-TURKEY*

Received 28.02.2001

By using 1-benzylpiperazinedithiocarbamate (1-BPzDC) as a new reagent, a method of solid-phase extraction is described for the pre-concentration of cadmium in water samples prior to its determination by flame atomic absorption spectrometry (FAAS). This method is based on the fact that cadmium forming in aqueous phase cadmium 1-benzylpiperazinedithiocarbamate complex ( $\text{Cd}(1\text{-BPzDC})_2$ ) can be extracted with microcrystalline naphthalene on solid phase, then back-extracted with potassium cyanide solution into aqueous phase and measured by FAAS. The optimum experimental parameters for the extraction and back-extraction of cadmium were investigated. The obtained recovery was nearly 97% when the enrichment factor was 500 for spiked cadmium solutions. The interfering effects of M(II), Fe(III), Cu(II), Ni(II), Pb(II), Cr(III), Hg(II), Zn(II), Bi(III), Ag(I), acetate, tartarate, oxalate, citrate, EDTA, cyanide, fluoride, chloride, bromide and iodide were investigated, and almost were eliminated except for EDTA and cyanide. The detection limit ( $0.034 \mu\text{g mL}^{-1}$ ) and the determination limit of the proposed method ( $0.114 \mu\text{g mL}^{-1}$ ) were evaluated as the concentration corresponding to three times and ten times the standard deviation of the blank signal, respectively.

**Key Words:** Solid-phase extraction, 1-benzylpiperazinedithiocarbamate, cadmium, flame atomic absorption spectrometry, microcrystalline naphthalene

## Introduction

The dithiocarbamate solid-phase-extraction method was applied to the pre-concentration of trace metals prior to their determination by AAS<sup>1-8</sup>. In these works, using traditional dithiocarbamates such as ammonium pyrrolidinedithiocarbamate (APDC), sodium diethyldithiocarbamate (NaDDC) and ammonium hexamethylene-dithiocarbamate (HMDC), metal dithiocarbamate complexes were constituted in aqueous phase and they were extracted on solid phase with activated carbon<sup>1,2,7</sup>, polyurethane foam<sup>4</sup>, microfiber filter<sup>5</sup>, silica gel<sup>8</sup>, or amberlite XAD resin<sup>3,6</sup>.

Hitherto, the effect of dithiocarbamate chelates on the adsorption of metal dithiocarbamates onto solid phase has been not studied. The mechanism for the adsorption of metal dithiocarbamates on solid phase is still under investigation<sup>1</sup>, but it is known that if the molecule size is increased, the adsorption, as a rule, is carried out easily<sup>9</sup>. From this point of view, it must be considered that the use of dithiocarbamate reagents which are large molecules may increase the efficiency of the extraction of metals.

In this study, NaDDC, a traditional reagent, potassium 4-methylpiperidinedithiocarbamate (K4-MPDC), potassium 1-methylpiperazinedithiocarbamate (K1-MPzDC), potassium 4-benzylpiperidinedithiocarbamate (K4-BPDC), potassium 1-benzylpiperazinedithiocarbamate (K1-BPzDC), potassium 1-(4-nitrophenyl)piperazinedithiocarbamate [K1-(4-NP)PzDC] and potassium 1-(4-fluorophenyl)piperazinedithiocarbamate [K1-(4-FP)PzDC] reagents were tested for the solid-phase extraction of cadmium in water samples prior to its determination by FAAS.

## Experimental

### Reagents and Apparatus

An ATI UNICAM 929 model flame atomic absorption spectrophotometer was used with the following conditions: 10 cm 1-slot burner, UNICAM cadmium hollow cathode lamp, wavelength: 228.8 nm, air-acetylene flame, fuel gas flow: 1.2 l/min, spectral bandwidth: 0.5 nm, burner height: 7mm, lamp current: 6 mA. All pH measurements were performed with a JENWAY 3040 model digital pH-meter. NaDDC was purchased from E. Merck and the potassium salts of other dithiocarbamic acids were prepared with the amines, carbon disulfide and potassium hydroxide at stoichiometric conditions according to the method given in the literature<sup>10</sup>. Reagent solutions were prepared with 0.5 g potassium salts of dithiocarbamic acids and 100 mL water. Cd(II) stock solution (1.000 mgmL<sup>-1</sup>) was prepared by dissolving the appropriate amount of cadmium nitrate (E. Merck, 99.5% ). Buffer solution was prepared with 0.1 mol acetic acid and 0.1 mol sodium acetate in 1000 mL deionized water. Deionized water was produced by ELGA Maxima Ultra Pure Water Systems. Certified reference material Zn/Al/Cu (43 X Z3 F) was provided by MBH Analytical Ltd. Other reagents were analytical reagent grade.

### Preparation of Microcrystalline Naphthalene

Naphthalene solution in acetone (100 mL 20% ) was injected in 500 mL deionized water, and the solid product was filtered by vacuum pump and washed with deionized water. It was dried in air for 10 to 15 min and stored in a flask as somewhat damp. If the naphthalene was dry, it became fixed on the top of the water solution during the extraction procedure of cadmium from 1000 mL water samples, and it was mixed with difficulty back into the solution.

### Solid – Phase Extraction Procedure

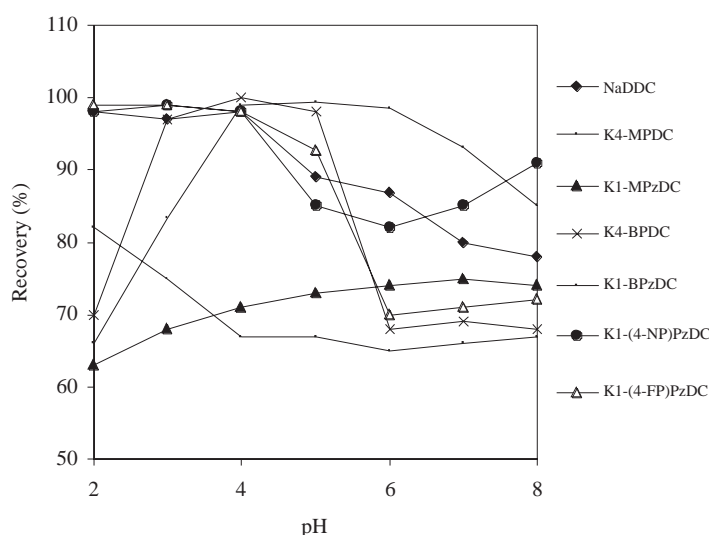
The solution of 1000 mL containing 0.5-30  $\mu\text{g}$  Cd(II) was taken in a flask and 1 mL 0.5% dithiocarbamate reagent solution was added and cadmium dithiocarbamate complex (Cd(DTC)<sub>2</sub>) was formed in aqueous phase. The pH of the solution was adjusted to between 4 and 5 after 10 mL buffer solution and 1 g microcrystalline naphthalene was added. The mixture was shaken vigorously for 10 min, then filtered by filter paper (Filtrax 391 Ref. Nr.: 3.104.125) and washed with deionized water. The solid product containing

cadmium complex was taken in a syringe and 2-5 mL potassium cyanide solution ( $0.1 \text{ mol L}^{-1}$ ) was added. It was shaken for 5 min, filtered by a syringe filter (Millipore SLMA-25 NB with pore-diameters of  $0.45 \mu\text{m}$ ) and aqueous phase was collected for measurement by FAAS.

## Results and Discussion

### Choice of Dithiocarbamate Reagent

Mixing 1 mL 0.5% reagent solution and cadmium solution, containing a certain amount of cadmium,  $\text{Cd}(\text{DTC})_2$  was formed in aqueous phase. Its pH was adjusted by  $\text{HNO}_3$  and  $\text{KOH}$  solutions. The procedure was applied and the concentration of the cadmium measured by FAAS. The recoveries for various dithiocarbamate reagents were calculated and the results are presented in Figure 1. The pH of the solution is important not only for extraction efficiency but also with regards side reactions. The pH should not go below 4 because of the fast decomposition of dithiocarbamate anion at low pH levels<sup>11</sup>. In addition, it is not selected over 7 in case metal hydroxides precipitate or their hydroxo complexes occur at high pH levels<sup>11</sup>. Therefore, K1-BPzDC is more suitable than other reagents between pH 4 and 6.



**Figure 1.** Effect of pH on the solid-phase extraction of cadmium on microcrystalline naphthalene with various dithiocarbamate reagents. Cadmium concentration:  $0.3 \text{ mgL}^{-1}$ , sample volume: 50 mL, back-extraction: 5 mL  $0.1 \text{ mol L}^{-1}$  potassium cyanide solution.

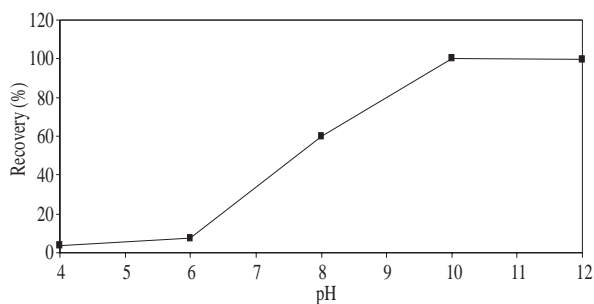
### Choice of Back-Extraction Procedure

The back extraction material is very important in the dithiocarbamate solid-phase extraction method. Usually, the metals extracted on the solid phase were eluted with isobutyl methyl ketone (IBMK) in organic phase<sup>4,8</sup> or with acid solution (nitric or hydrochloric acid) into aqueous phase<sup>1-3,5-7</sup>. In addition, metal solutions such as  $\text{Hg}(\text{II})$ <sup>12</sup> or complexing agents such as potassium cyanide<sup>13</sup> can be used. From the point of view of efficiency, selectivity and time, potassium cyanide is more suitable than others<sup>13</sup>.

At the beginning of this study, alternatively, EDTA was tested as back-extraction material, but it was found that the recovery from it was very poor. Finally,  $0.1 \text{ mol L}^{-1}$  potassium cyanide solution was

selected<sup>13</sup>. The effect of pH on the back extraction was studied as follows:

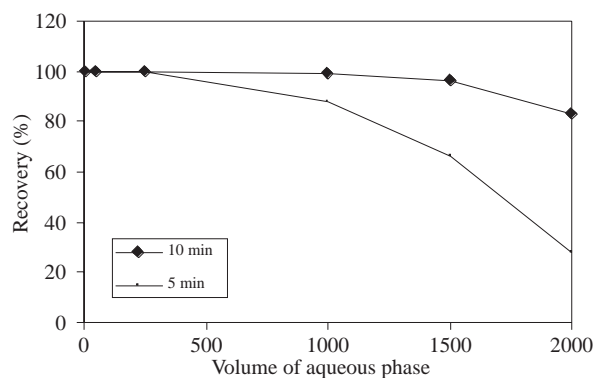
The cadmium, adsorbed on solid phase according to the procedure, was back-extracted with the potassium cyanide solution while adjusting pH by HNO<sub>3</sub> and KOH and it was measured by FAAS. The results are given in Figure 2. It was detected that back-extraction efficiency was nearly 100% when the pH was above 10.



**Figure 2.** Effect of pH on the back-extraction of cadmium with 0.1 mol L<sup>-1</sup> potassium cyanide solution. Extraction: cadmium concentration: 0.3 mgL<sup>-1</sup>, sample volume: 50 mL, back-extraction: 5 mL 0.1 mol L<sup>-1</sup> potassium cyanide solutions at different pH levels.

### Effect of Volume of the Aqueous Phase

The solutions containing 5  $\mu$ g cadmium were diluted from 50 to 4000 mL by deionized water and analyzed by the procedure mentioned. The results are given in Figure 3. It was determined that the extraction recovery of cadmium did not vary up to 1500 mL for 10 min extraction time. It was selected to be 1000 mL for confidence.



**Figure 3.** Effect of the volume of aqueous phase for the extraction of cadmium with K1-BPzDC reagent. Cadmium 5  $\mu$ g in different volumes from 5 to 2000 mL of aqueous solutions, back-extraction: 2 mL 0.1 mol L<sup>-1</sup> potassium cyanide solution.

### Effect of the Diverse Ions

A sample solution of 100 mL containing 3  $\mu$ g cadmium and different alkali metal salts or metal ions was prepared. The determination of cadmium was carried out according to the general procedure described above. It was observed that only cyanide and EDTA strongly interfered in the adsorption of cadmium on microcrystalline naphthalene because they form highly stable complexes with cadmium. Other salts and

metal ions can be tolerated up to milligram per mL levels. The tolerance limits (amount of salts or metal ions of varied absorbance of cadmium in FAAS  $\leq 3\%$ ) are given in Table 1.

**Table 1.** Tolerance limits for diverse metal ions and salts in  $30 \mu\text{gL}^{-1}$  cadmium solution.

<i>Salt</i>	<i>Tolerance limit*</i> ( $\text{mgmL}^{-1}$ )	<i>Metal ion</i>	<i>Tolerance limit*</i> ( $\text{mgmL}^{-1}$ )
Sodium acetate	>1	Mn(II)	> 3
Sodium tartarate	>1	Fe(III)	> 3
Sodium oxalate	0.7	Cu(II)	1.8
Sodium citrate	>1	Ni(II)	> 3
Disodium EDTA	—	Pb(II)	2.1
Potassium cyanide	—	Cr(III)	> 3
Sodium floride	250	Hg(II)	1.2
Sodium chloride	160	Zn(II)	> 3
Sodium bromide	210	Bi(III)	> 2.5
Sodium iodide	24	Ag(I)	2.2

\* Tolerance limit is the maximum amount in which them is less than 3% effect on absorbance.

### Calibration Curve, Detection Limit, Determination Limit and Recovery

The calibration graph was constructed at 228.8 nm with six standard solutions according to the general procedure. It was linear over the concentration range  $0\text{-}3 \mu\text{g mL}^{-1}$  of cadmium in the final potassium cyanide solution. The correlation coefficient (0.9992) was obtained with the method of least squares. The detection limit ( $0.034 \mu\text{g mL}^{-1}$ ) and the determination limit ( $0.114 \mu\text{g mL}^{-1}$ ) were evaluated as the concentration corresponding to three times and ten times the standard deviation of the blank signal, respectively. The recoveries for standard cadmium solutions and spiked sample solutions are presented in Table 2.

**Table 2.** The recoveries of cadmium in spiked water samples.

Sample	Taken Cd ( $\mu\text{gL}^{-1}$ )	Found * ( $\mu\text{gL}^{-1}$ )	Recovery %
Deionized water	10.00	9.76	$97.60 \pm 3.6$
	20.00	19.41	$97.05 \pm 4.0$
	30.00	29.62	$98.73 \pm 3.9$
Tap water	-	$0.137 \pm 0.018$	
	10.00	9.83	$98.30 \pm 4.7$
	20.00	19.28	$96.40 \pm 3.5$
	30.00	29.14	$97.13 \pm 2.9$
Sea water	-	$0.280 \pm 0.033$	
	10.00	9.94	$96.69 \pm 5.4$
	20.00	20.02	$98.79 \pm 5.7$
	30.00	29.58	$97.6 \pm 5.1$

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

Samplpe volume: 1000 mL, microcrystalline naphthalene: 1g, extraction time: 10 min, potassium cyanide volume: 2 mL ( $0.1 \text{ mol L}^{-1}$ ), back-extraction time: 5 min and enrichment factor: 500.

### Determination of Cadmium in Standard Metal Alloy

A 1.0000 g sample of the alloy was taken in a 100 mL beaker and 20 mL concentrated  $\text{HNO}_3$  was added. The mixture was heated on a hot plate until it was nearly dry. After the addition of 5 mL nitric acid, it was

diluted with deionized water. It was filtered and made up to 1000 mL in a standard flask. An aliquot of the solution of alloy was taken, the pH was adjusted to 4-5 adding acetate buffer and the amount of cadmium was determined by the same procedure. The results are given in Table 3.

**Table 3.** Determination of cadmium in standard alloy.

Standard metal alloy	Certified composition (%)	Taken Cd* ( $\mu\text{g}$ )	Found** ( $\mu\text{g}$ )
Zn / Al / Cu 43 X Z3 F	Pb : 0.027 Mg : 0.10 Al : 4.0 Fe : 0.085 Sn : 0.006 Cu : 1.41 Ni : 0.018 Mn : 0.001 <b>Cd : 0.003</b>	6.00	6.34 $\pm$ 0.42

\* 200 mL standard cadmium alloy solution (30  $\mu\text{gL}^{-1}$ ) was taken, it was diluted with deionized water up to 1000 mL and cadmium determined according to the procedure.

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

## Determination of cadmium in water samples

Tap water samples were obtained from Ondokuz Mayıs University and seawater samples were obtained from the coast of Samsun (Black Sea). The samples were filtered, the pH was adjusted adding acetate buffer and they were analyzed by the same procedure. The results are given in Table 2.

## Conclusion

The rate of decomposition for the reagent is directly proportional to the hydrogen ion concentration. As the dithiocarbamates are unstable in acidic media, pH adjustment and buffer addition are often necessary. (The half-lives of the diethyldithiocarbamic acid at pH 4, 5, 6 and 7 at room temperature are 0.5, 4.9, 51 and 498 min respectively<sup>14</sup>). On the other hand, although metal-dithiocarbamate complexes are more stable than dithiocarbamic acids, the stability of them decreases in acidic media too. (The half-lives of lead-hexamamethylenedithiocarbamate in 0.001, 0.01, 0.1 and 1 mol L<sup>-1</sup> HCl solution are 600, 360, 300 and 240 min, respectively<sup>15</sup>). Use of K1-BPzDC as a chelating agent for the pre-concentration of cadmium increases extraction efficiency between pH 4 and 6, which is most suitable for the extraction of cadmium, in comparison with other reagents. Therefore, the effect of dithiocarbamate reagent must be considered like other parameters in solid-phase extraction studies.

In this study, the enrichment factor is 500 (1000 mL sample, 2 mL final potassium cyanide solution). If a larger sample volume is taken or microcrystalline naphthalene, which is produced at the several extraction procedure, is gathered the enrichment factor can be increased in the samples containing lower cadmium concentrations. Moreover, the gathered naphthalene can be sublimated in a oven above 80 °C and the volume of potassium cyanide solution can be decreased in back-extraction.

The proposed method for the determination of cadmium in water samples is very selective because the dithiocarbamates do not react with alkali and earth alkali metals that were fairly abundant in environmental samples; moreover, K1-BPzDC contributes some advantages. In addition, potassium cyanide solution increases selectivity in back-extraction for cadmium because cyanide ions do not react with many metals.

Thus, the method is simple, selective, sensitive and accurate. It can be used for the determination of cadmium in water samples, alloys and other materials.

### References

1. G.R. Boventura, S.R. Hirson, R.E. Santelli, **Fresenius J. Anal. Chem.**, **350**, 651-652, (1994).
2. M. Soy lak, L. Elçi, M. Doğan, **Fresenius Environ Bull.**, **3-4**, 148-155, (1996).
3. M. Soy lak, L. Elçi, **Int. J. Environ Anal. Chem.**, **1**, 51-59, (1997).
4. S. Arpadjan, L. Vuchkova, E. Kostadinova, **Analyst**, **122**, 243-246, (1997).
5. Z. Aneva, S. Stamov, S. Kaleydjieva, **Anal. Lab.**, **6, 2**, 67-71, (1997).
6. K. Anezaki, X.Z. Chen, T. Ogasavama, I. Nukatsuka, K. Ohzeki, **Anal. Sci.**, **14, 3**, 523-527, (1998).
7. M. Soy lak, **Fresenius Environ Bull.**, **7-8**, 383-387, (1998).
8. I. Karadjova, **Mikrochim Acta**, **3**, 185-190, (1999).
9. M. Campbell, *Catalysis at Surfaces*, Hapman and Hall, London (1987).
10. B. Batý, H. Cesur, H. Batý, M. Özdemir, **Turk J Chem.**, **19, 1**, 66-72, (1995).
11. A. Hulanicki, **Talanta**, **14**, 1371-1392, (1967).
12. H. Cesur, M. Macit, B. Batı, **Anal. Lett.**, **33, 10**, 1991-2004, (2000).
13. H. Cesur, B. Batı, **Anal. Lett.** **33, 3**, 489-501, (2000).
14. J. Stary, *Solvent Extraction of Metal Chelates*, Pergamon Press Ltd. London (1964).
15. A.R.K. Dapaah, N. Takono, A. Ayame, **Anal. Chim. Acta**, **386**, 281-286, (1999).