



## Determination of Cadmium by Electrothermal Atomic Absorption Spectrometry Using Single Drop Micro Extraction in Real Samples

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In this investigation a novel and extremely sensitive method for extraction and determination of cadmium in aqueous samples by liquid phase micro extraction combined with electrothermal atomic absorption spectrometry using a new ligand is described. In this method  $\text{Cd}^{2+}$  in pH 4 during 20 min extraction time at 20 °C is reacted with S-methyl-3-salicylidene dithiocarbamate dissolved in 4  $\mu\text{L}$  of chloroform micro drop. After extraction, the micro drop was retracted and directly transferred into a graphite tube coated by palladium as chemical modifier. In this investigation the type of organic solvent, volume of organic solvent, pH, temperature and extraction time were optimized. Using 10 mL sample solution an enrichment factor of 100 was obtained. The detection limit was calculated to be 6  $\text{pg mL}^{-1}$  based on  $3S_b$ , and relative standard deviation for five replicate analysis of 0.2  $\text{ng mL}^{-1}$   $\text{Cd}^{2+}$  was 4.9 %. The calibration curve was linear in the range of 6  $\text{pg mL}^{-1}$  to 1.0  $\text{ng mL}^{-1}$  with a sensitivity of 1.0  $\text{pg mL}^{-1}$ . This method was used for determination of cadmium in tap water, waste water, sea water, soil and reliability of the method was evaluated using two reference materials.

**Key Words:** Cadmium, Electrothermal atomic absorption spectrometry, Liquid phase, Micro extraction, Chemical modifier, S-Methyl-3-salicylidene dithiocarbamate.

### INTRODUCTION

Cadmium is an important element and its determination is of great importance. It is 20th most abundant element in the earth's crust. In addition to drinking water, humans are exposed to a considerable amount of cadmium through food and various cadmium species which are present in the environmental and biological systems. Their low concentrations and differences in their toxicities, biological and environmental behaviours require sensitive methods for the determination of these individual species. Considerable analytical progress has been made toward sensitive methods of analytical determination and speciation over the last decades. In order to determine trace levels of elements an extraction and pre-concentration step is necessary. Conventionally, this can be accomplished by liquid-liquid extraction (LLE). However, liquid-liquid extraction is time consuming, tedious, requires too much of organic solvent and can be relatively expensive. Recently solid phase extraction (SPE) has gained favour as a replacement for liquid-liquid extraction, using low amounts of organic solvent and capability of automation. Solid phase microextraction (SPME) was proposed in 1989 by Pawliszy *et al.*<sup>1</sup>. For SPME a small dimension fused silica fibre coated with a high temperature

phase is applied, having the advantages of a higher enrichment factor, free of solvent and risk of contamination and ease of application to field sampling and automation. Chamsaz *et al.*<sup>2</sup> developed a newly method, liquid phase microextraction (LPME) which overcomes the problems of solvent evaporation (LLE, SPE) and fibre preparation in SPME. It is based on the traditional LLE technique but involves only a few microliters of organic solvent as an extractant. This method is quick, inexpensive and uses small volume of organic solvents. This technique employs a simple equipment which is found in most analytical laboratories and is used for preconcentration of organic components and has been coupled with chromatography and spectroscopy methods<sup>2-4</sup>. In this work the LPME method is reported for determination of cadmium in a variety of samples. Despite the advantages of this method, no work has been reported so far on the coupling of LPME with spectrometry to determine inorganic compounds. Bueno and Potin- Gautier applied the SPE technique using Amberlite resin followed by high performance liquid chromatography<sup>5</sup>. Komarek *et al.* reported a method for extraction and determination of cadmium. In this method cadmium is extracted in a microcell by applying an electrical current and then determined by electrothermal atomic absorption spectrometry<sup>6</sup>. Also many chemical modifiers

have been reported for determination of cadmium by ETAAS. The best chemical modifier was palladium coated in graphite tube<sup>7-12</sup>.

## EXPERIMENTAL

All reagents were of analytical reagent grade and triply distilled water was used throughout and ligand was prepared with the following method.

**Preparation of S-methyldithiocarbamate:** S-methyldithiocarbamate was prepared as previously reported<sup>13</sup>. A mixture of KOH (22.8 g, 0.4 mol) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (20 g, 0.4 mol) in 90 % ethanol (140 mL) was cooled down to 5 °C. CS<sub>2</sub> (30.4 g, 0.4 mol) was added dropwise with stirring. The temperature was kept below 5 °C all the time. Two layers were foamed and the yellow oil was separated and dissolved in 40 % ethanol (60 mL) and the solution was cooled in ice bath.

Methyl iodide (58 g, 0.4 mol) was added slowly with vigorous stirring. The white product was separated by filtration, washed with water and dried in air. The crude product was recrystallized in ethanol; yield: 40 %; m.p. 82 °C.

**Preparation of S-methyl-3-salicylidene dithiocarbamate (SMSDC):** This compound was prepared as previously reported<sup>14</sup>. S-methyldithiocarbamate (2.4 g, 0.2 mol) was dissolved in 50 mL of hot ethanol. To this solution was added 2.45 g (21.5 mL 0.2 mol) of salicylaldehyde in 50 mL ethanol. The resultant mixture was heated on a steam bath for *ca.* 15 min. The precipitate crystals, were filtered off, washed with ethanol, recrystallized in benzene and dried *in vacuo*. Yield: 80 %; m.p. 210 °C.

A stock 1000 ppm of cadmium solution was prepared by dissolving appropriate amounts of CdSO<sub>4</sub>·H<sub>2</sub>O in 1 % HNO<sub>3</sub>. 0.1 % (w/v) Pd prepared by dissolving PdCl<sub>2</sub> in HCl 2 % was used as chemical modifier for coating of graphite tubes. 0.2% (w/v) S-methyl-3-salicylidene dithiocarbamate in chloroform was used as acceptor phase.

A 10 µL Hamilton syringe was used to suspend the drop of the acceptor phase and to inject it into the graphite furnace atomizer.

A Shimadzu model AA-670 atomic absorption spectrometer with GFA-4B graphite furnace atomizer and D<sub>2</sub> lamp for background correction was used.

Cadmium hollow cathode lamp was used as radiation source adjusted at 4 mA. An atomic absorption signal at 228.8 nm line was recorded on a graphic printed PR-4 with peak height and gas stop mode for quantification. The temperature program for the furnace is given in Table-1.

TABLE-1  
GFA HEATING PROGRAM

Stage	Furnace temp. (°C)	Mode	Time (s)	Argon flow rate (L min <sup>-1</sup> )
Drying	150	Ramp	15	1.5
Ashing	400	Step	15	1.5
Atomization	1800	Step	3	0 (gas stop)
Cleaning up	2200	Step	2	1.5

**Determination of cadmium via preconcentration using 'Single drop micro extraction' technique:** 10 mL of Cd(II) solution was adjusted at pH 4 and transferred into a 15 mL vial. The vial was maintained at a temperature of 20 °C in

water-bath and Cd(II) was extracted into a 4 µL chloroform drop containing 0.2 % (w/v) SMSDC on the tip of a Hamilton syringe for 20 min. The solution was stirred (500 rpm) during the extraction (Fig. 1).

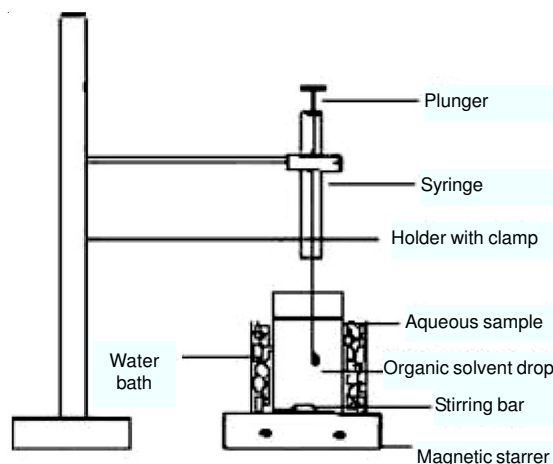


Fig. 1. Schematic setup for single drop micro extraction

After the extraction was completed, the organic phase was directly injected into the graphite tube coated by 60 µL 0.1 % (w/v) Pd as chemical modifier.

## RESULTS AND DISCUSSION

**Optimizing the parameters for extraction:** In order to investigate the effects of different parameters on pre-concentration of cadmium by single drop micro extraction, 10 mL solution of 0.2 ng mL<sup>-1</sup> cadmium was used at all the following stages:

**Solvent:** Different solvents were tested from the volatility and dissolving points of view such as chloroform, dichloromethane, dichloroethane, nitrobenzene and carbon tetrachloride. Chloroform showed the best results for extraction of cadmium complex (Fig. 2).

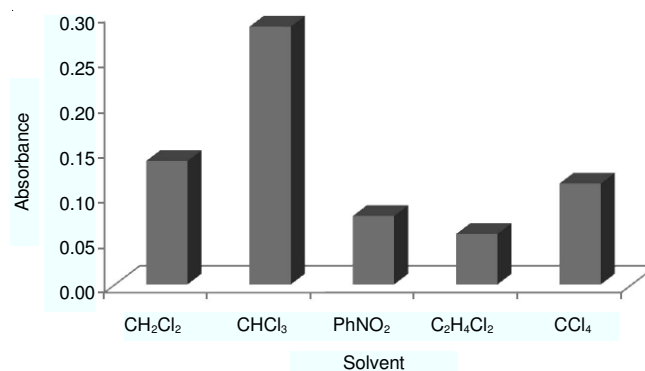


Fig. 2. Effect of solvent

**pH:** The extraction efficiency of the method was tested at different pH. As can be seen from Fig. 3, the best pH was 4. At pH lower than 4, protonation of the nitrogen atoms in ligand molecules occurs and complexation strength of Cd<sup>2+</sup> is decreased. At pH higher than 4, cadmium ions are hydrolyzed and extraction efficiency is decreased.

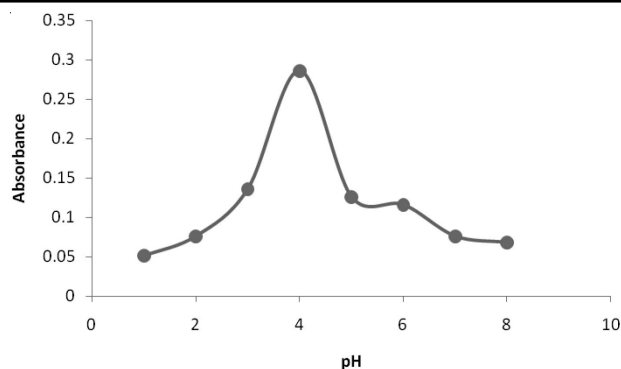


Fig. 3. Effect of pH

**Ligand concentration in organic phase:** The ligand (SMSDC) concentration in organic phase was varied from 0.02 to 0.4 % (w/v) using 10 mL  $\text{Cd}^{2+}$  at pH 4. The extraction efficiency was increased with increasing of the ligand concentration up to 0.2 % (w/v) and then leveled off at higher concentrations (Fig. 4). As the results show the optimum concentration of ligand is 0.2 % (w/v).

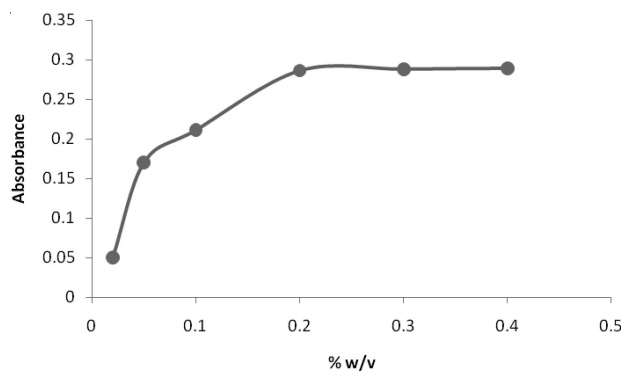


Fig. 4. Effect of ligand concentration

**Temperature:** The extraction of complex into the drop was performed in the range of 5-30 °C and the results show an optimum temperature of 20 °C and maximum efficiency was attained in this temperature (Fig. 5). In low temperatures the formation constant ( $K_f$ ) of metal complex is decreased and at high temperatures, the partition coefficient in two phases and also the organic phase volume are decreased.

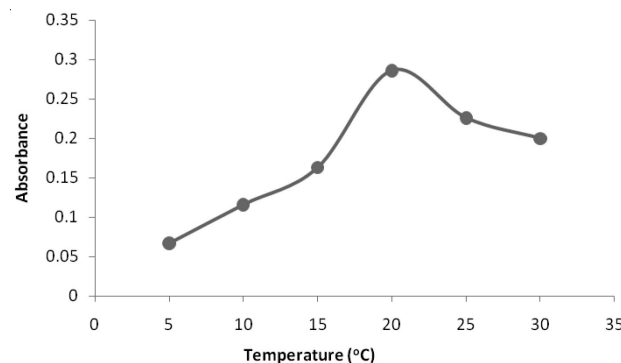


Fig. 5. Effect of temperature

**Extraction time:** The time of extraction was varied from 2 to 30 min. By increasing the extraction time, the extraction of cadmium complex into the drop is increased. However

after 20 min the drop becomes saturated with the cadmium complex and the extraction efficiency attains constancy (Fig. 6). As the results show the optimum extraction time is 20 min.

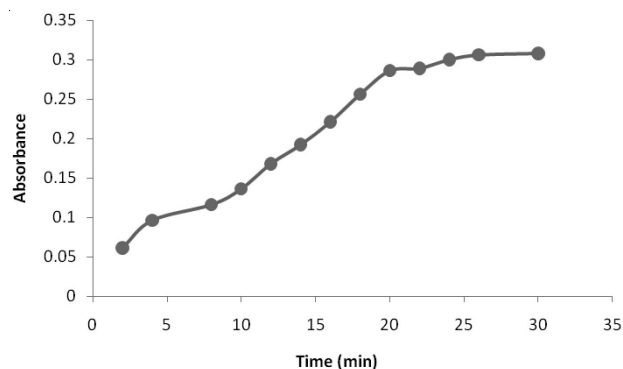


Fig. 6. Effect of time

**Volume of aqueous and organic phase:** Changing the organic volume from 1 to 4  $\mu\text{L}$  increased the extraction efficiency. However higher volumes were avoided due to mechanical instability. 10 mL solution volume was chosen for the analysis as lower volumes caused falling of the drop due to agitation and higher volumes showed no benefit for the extraction process and were not used.

**Effect of ionic strength and salt concentration:** The effect of ionic strength was tested using potassium chloride in the concentration range of 0.02 to 0.25  $\text{mol L}^{-1}$  (Fig. 7).

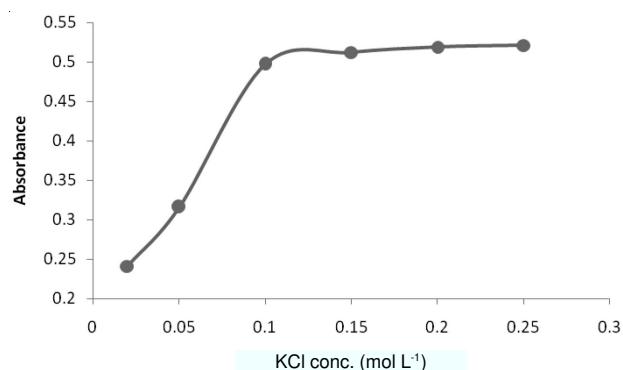


Fig. 7. Effect of ionic strength

At high concentrations of salt, solvent molecules are in contact with salt ions and  $\text{Cd(II)}$  ions are relatively free in the solution for complexation. By this action, the efficiency of extraction is increased but higher concentration of salt than 0.1  $\text{mol L}^{-1}$  decreases this effect and the extraction efficiency becomes constant.

**Effect of interferences:** Interfering species at 100 fold excess were added to  $\text{Cd(II)}$  solution and the extraction was followed at the optimized conditions. Table-2 shows the results. The serious interferences are due to  $\text{Bi}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Ag}^+$  and  $\text{Au}^{3+}$  which could be effectively removed by using separate solutions of 0.1 M KCN for  $\text{Au}^{3+}$ ,  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ , 0.1 M NaF for  $\text{Bi}^{3+}$  and 0.1 M tartaric acid for  $\text{Sb}^{3+}$ .

**Analytical figures of merit:** Calibration curve was constructed at the optimized conditions and was linear in the range of 6  $\text{pg mL}^{-1}$  to 1.0  $\text{ng mL}^{-1}$  cadmium with a correlation coefficient of 0.9988 and sensitivity of 1.0  $\text{pg mL}^{-1}$ . The detection

TABLE-2  
EFFECT OF INTERFERING IONS

Interfering ion*	% Relative error in absorbance	Interfering ion*	% Relative error in absorbance
Cl <sup>-</sup>	0.8	Sn <sup>4+</sup>	-2.1
NO <sub>3</sub> <sup>-</sup>	-0.2	Sb <sup>3+</sup>	-18.3
PO <sub>4</sub> <sup>3-</sup>	-1.6	Cr <sup>3+</sup>	-1.6
SO <sub>4</sub> <sup>2-</sup>	-0.3	Cu <sup>2+</sup>	-4.3
AsO <sub>3</sub> <sup>3-</sup>	-1.0	Hg <sup>2+</sup>	-10.8
SiO <sub>3</sub> <sup>2-</sup>	-2.3	Pb <sup>2+</sup>	-1.7
Na <sup>+</sup>	3.6	Fe <sup>3+</sup>	-5.1
K <sup>+</sup>	3.3	Zn <sup>2+</sup>	-2.8
Mg <sup>2+</sup>	-1.2	Ag <sup>+</sup>	-11.7
Ca <sup>2+</sup>	-0.2	Mn <sup>2+</sup>	-0.6
Bi <sup>3+</sup>	-21.6	Co <sup>2+</sup>	-0.9
Ba <sup>2+</sup>	-1.6	Ni <sup>2+</sup>	-1.3
Al <sup>3+</sup>	-3.2	Au <sup>3+</sup>	-51.2

\*The solutions for cations is preparation of chloride salts and also anions preparation of sodium salts.

limit was calculated to be 6 pg mL<sup>-1</sup> based on 3S<sub>b</sub>. The relative standard deviation (RSD) for five replicate analysis of 0.2 ng mL<sup>-1</sup> cadmium was 4.9 %. Recovery test was performed using tap water, waste water, sea water with 0.2 ng mL<sup>-1</sup> cadmium and 10 µg g<sup>-1</sup> cadmium for spiked soil sample. The result shows a recovery of 95-105 % for the technique.

**Analysis of real sample:** In order to evaluate the capability of the method different real samples and reference materials were analyzed according to the method described earlier. The results are given in Tables 3 and 4.

TABLE-3  
RESULTS OF DETERMINATION CADMIUM IN REAL SAMPLES

Sample	Cd added (ng mL <sup>-1</sup> )	Cd added (ng mL <sup>-1</sup> )	Recovery (%)
Tap water	0	0	-
	0.20	0.21 ± 0.08	105
Wastewater	0	0.15 ± 0.05	-
	0.20	0.34 ± 0.06	95
Sea water	0	0.08 ± 0.02	-
	0.20	0.29 ± 0.04	105
Soil sample	0	17.6 µg g <sup>-1</sup> ± 0.5	-
	10.0 µg g <sup>-1</sup>	27.8 µg g <sup>-1</sup> ± 0.8	102

TABLE-4  
RESULTS OF DETERMINATION CADMIUM IN REFERENCE MATERIALS

Reference material	Reported value (µg g <sup>-1</sup> )	Determination value (µg g <sup>-1</sup> )	Recovery (%)
JSL-1	0.118	0.117 ± 0.08	99
JSd3	1.045	1.050 ± 0.40	100

## Conclusion

The results show a very promising technique for determination of cadmium in a variety of samples at ng mL<sup>-1</sup> and pg mL<sup>-1</sup> levels without the needs for any sophisticated device. Apart from having extremely high sensitivity, the procedure is very simple, nearly fast and benefits a very low detection limit. By the use of a preliminary separation step using a resin, the method could be relatively free from interferences. The experimental parameter such as chemical modifier, organic solvent, pH of aqueous phase, sampling temperature, extraction time, volume of aqueous and organic phase and ionic strength have great effects on the sensitivity of method and should be optimized. The results show that cadmium could be determined with very high sensitivity and relatively good reproducibility in aqueous samples such as tap water, sea water, waste water and solid samples.

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