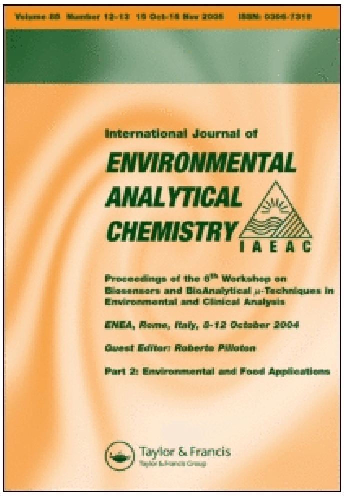

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The use of solid-phase extraction and direct injection of a copolymer sorbent as slurry into the graphite furnace prior to determination of cadmium by ETAAS

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Cadmium in different certified materials was determined by direct injection of sorbent loaded with the analyte into the graphite furnace of electrothermal atomic absorption spectrophotometer. For this purpose, cadmium was collected on ethylene glycol dimethacrylate-methacrylic acid copolymer treated with ammonium pyrolidine dithiocarbamate by the batch technique. After separation of liquid phase, slurry of the sorbent was prepared for the direct injection of the sorbent into graphite furnace. Optimum conditions for quantitative sorption and those for preparing homogeneous and durable slurry were investigated. A 100-fold enrichment factor could be reached. Cadmium in certified sea water and bovine liver samples was determined within the 95% confidence limits. The proposed technique is fast and simple, and the risk of contamination is low. The calculated detection limit for cadmium using sample-matching blanks was $0.09\,\mu g\,L^{-1}$ according to the 3σ concept for the described method.

Keywords: Separation; Preconcentration; Cadmium; Electrothermal atomic absorption spectrometry; Slurry sampling

1. Introduction

Cadmium is one of the non-essential toxic metals in the earth's crust and oceans and present everywhere in air, water, soils, and foodstuffs. It occurs naturally in the environment from the gradual process of erosion and abrasion of rocks and soils, and from singular events such as forest fires and volcanic eruptions. Cadmium and several cadmium-containing compounds are known carcinogens, can cause adverse human health effects in the lungs and kidneys, and can induce many types of cancer. Cadmium is also a potential environmental hazard. Human exposures to environmental cadmium are primarily the result of the burning of fossil fuels and municipal wastes. However, there have been notable instances of toxicity as the result of long-term exposure to cadmium in contaminated food and water. Therefore, cadmium should be at a minimum level in all matrices, and its determination of cadmium at concentrations as

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low as possible is important. Electrothermal atomic absorption spectrometry (ETAAS) is an important tool for the determination of trace elements. However, when the concentration of the analyte is too low to be determined directly and/or interferences due to matrix cannot be eliminated, the use of a separation/preconcentration technique is a necessity. For this purpose, the most commonly and practically applied method is the collection of the analyte on a sorbent using different materials such as Chromosorb [1], polymeric resins [2], silica [3], rice husk ash [4], activated bentonite [5], Amberlite XAD-7 [6], activated carbon with or without chelating groups [7, 8], and subsequently its elution by means of a convenient reagent. However, in almost all of these, an elution step was necessarily applied in order to transfer the analyte into solution phase for its convenient measurement. Elution is a critical and limiting step with respect to loss of time, risk of contamination, high blank values, and quality of analytical data such as recovery, precision, enrichment of analytes, etc. It should be fast, complete, and reproducible. The reagents used for elution, usually moderately concentrated acids, may decrease the lifetime of graphite tubes. Therefore, the elution step determines the appropriateness of the method including fastness, easiness, accuracy (or recovery), and precision very strongly. In order to avoid an elution step, Nukatsuka *et al.* [9] developed a 'mini' solid-phase extraction system. In this system, cellulose nitrate resin, on which thallium was collected, was suspended in a small volume of aqueous solution and was directly introduced into the furnace using the conventional liquid-sample delivery technique. The introduction of solid samples as their suspensions directly into graphite furnace (slurry technique) has many advantages in AAS. In the slurry method, solid samples are first finely ground, slurried with an appropriate liquid mostly adding surfactants, e.g. Triton-X 100, homogenously mixed manually or using tools such as ultrasonic agitation, and finally pipetted into the furnace by means of a micropipette or autosampler. In this technique, the duration of sample preparation is very short, and only very small amounts of reagents are used. In addition, the enrichment factor can be adjusted by modifying the volume of the suspension. The smaller the volume of suspension, the greater the enrichment factor attained. Therefore, ultra-trace concentrations can be detected. However, to obtain a homogeneous and stable slurry, which has a direct influence on the accuracy and precision, many experimental parameters such as particle size, solid to total slurry volume, addition of stabilizing agent, etc. should be optimized. The slurry sampling technique has been extensively used for the determination of trace elements in different samples such as sodium and iron in single crystals of rubidium titanyl phosphate [10]; copper in sediments [11]; selenium, cadmium, and lead in different types of baby foods using slurried samples [12]; lead in several fish samples [13]; and lead, cadmium, and copper in mineral coal [14] and in cervine liver and kidney [15].

In this study, in order to obtain higher enrichment factors and to avoid the drawbacks of the elution step, sorption by the batch technique and the slurry method were combined. For this purpose, cadmium was sorbed on ethylene glycol dimethacrylatemethacrylic acid copolymer (EGDMA-MA) treated with ammonium pyrolidine dithiocarbamate (APDC) by the batch technique. After separation of the liquid phase, the sorbent loaded with analyte was slurried appropriately and pipetted directly into the graphite furnace. The effects of experimental parameters on the sorption of analyte as well as the optimum conditions to obtain an homogeneous and stable slurry were investigated. This work is the combination of sorption and

Table 1. Graphite furnace programme for the determination of Cd for aqueous solutions as well as Sea water and Bovine Liver samples[a].

Step no.	Step (furnace temperature,°C)	Time (s) Ramp	Time (s) Hold	Internal gas flow ($mL\,min^{-1}$)	Read
1	Drying (110)	10	15	300	–
2	Drying (150)	5	15	300	–
3	Pyrolysis (600)	10	20	300	–
4	Atomization (2300)	0	6[b]	50	c
5	Cleaning (2650)	1	5	300	–
6	Cooling (20)	2	6	300	–

[a] In the presence of [0.2 mg $NH_4H_2PO_4$ and 0.01 mg $Mg(NO_3)_2$] as a modifier.
[b] Even 3 s was sufficient for the completion of the atomization.
[c] Absorbance was read.

slurry techniques. EDGMA-MA was suitable both to collect the analyte and to prepare a homogeneous slurry that would be stable for a reasonable amount of time.

2. Experimental

2.1 *Apparatus and reagents*

A Perkin-Elmer 3030 Zeeman atomic absoption spectrophotometer equipped with an HGA-600 graphite furnace was used for the determination of cadmium. Pyrolytic graphite-coated tubes with pyrolytic L'vov platforms were used throughout this work. The wavelength was set to 228.8 nm for cadmium. The graphite furnace programme for the determination of cadmium using [0.2 mg $NH_4H_2PO_4$ and 0.01 mg $Mg(NO_3)_2$] as the modifier is given table 1.

The pH of the sample was adjusted by 0.01 $mol\,L^{-1}$ NH_4OH or 0.01 $mol\,L^{-1}$ HNO_3 and controlled using a WTW pH 340-A/SET2 pH meter. All chemicals were of analytical reagent grade (Merck, Germany). Stock solution (1000 $mg\,L^{-1}$) of Cd was prepared from Titrisol concentrates (Merck) and further diluted with distilled-deionized water daily. EGDMA-MA was synthesized in the laboratory as described elsewhere [16]. Ammonium pyrolidine dithiocarbamate (APDC) was purchased from Fluka, whereas sea water (CRM-SW) and bovine liver (CRM-BL) certified reference materials were bought in solution form from High-Purity Standards (Charleston, SC). Samples were introduced into the graphite furnace manually in a volume of 10 μL with an Eppendorf micropipette. Results were given as the averages of at least three independent replicate analyses.

2.2 *Procedure for slurry sampling*

EGDMA-MA, used as the sorbent, was finely ground and sieved as 50 mesh. It was washed three times with 10 mL of 0.1 $mol\,L^{-1}$ NaOH, then three times with 10 mL of 0.1 $mol\,L^{-1}$ HCl, and finally three times 10 mL of distilled-deionized water consecutively until no analyte was determined in the washing, and dried at 100°C overnight. Fifty milligrams of sorbent was treated with 10 mL of 0.05% (w/v) APDC, and the liquid phase was removed by vaporization. In order to collect the analyte by the batch technique, 50 mg of sorbent treated with APDC was weighed precisely and the solution mixed with 40 mL of sample solution including a minimum of 0.3 $\mu g\,L^{-1}$ of Cd. The pH of the solution was adjusted to 6.5 manually and shaken for 5 min. The solid part was precipitated by centrifugation for 5 min at 1000 rpm. It should be noted once again that bovine liver CRM was bought as a solution (not solid). Therefore, a digestion procedure for bovine liver CRM was not given. The supernatant was removed by decantation. The sorbent, collecting the analyte, was washed with water a few times to remove the matrix traces, and washing water was removed by decantation also. The slurry of the sorbent carrying analyte (minimum 0.3 $\mu g\,L^{-1}$ Cd) was prepared in 400 µL of 1% Triton X-100 and homogenized further manually in the autosampler cup by stirring with a micropipette tip just before each sampling. The slurry was then pipetted manually with 10 µL of pipette into the graphite furnace and atomized, applying the graphite furnace programme given in table 1.

It should be noted that after 100-fold concentrations, the sensitivity with gas-stop mode during the atomization step was too high, and a mini-gas flow of 50 $mL\,min^{-1}$ was applied in order to reduce the sensitivity. Another alternative would have been dilution of slurry, but since we are limited by the ratio of solid amount to total slurry volume, we preferred to use mini-gas flow as the most appropriate solution.

3. Result and discussion

The procedure described in this study is the combination of sorption and slurry techniques. The sorbent should quantitatively and rapidly collect the analyte from large volumes in a large pH range, and blank values should be low. In addition, a homogeneous slurry of the sorbent remaining stable could be easily prepared, and it should stay homogeneous during the whole analysis with minimum effort. It should be mentioned that most of the sorbents cannot meet this requirement. EGDMA-MA is a new sorbent and was synthesized in the laboratory. Since EDGMA-MA was suitable both to collect the analyte and to prepare a homogeneous slurry lasting stable in a reasonable duration of time, it was selected as a sorbent material in this work. Thus, in order to obtain quantitative recovery and high precision, both sorption and slurry parameters were carefully optimized. Therefore, first of all, quantitative sorption of cadmium onto the sorbent is a prerequisite which depends on the pH of the sample, sample volume, amount of sorbent, shaking time, addition of chelating agent (if necessary), etc. In addition, the success of the slurry technique necessitates a careful selection of solid-phase material, convenient mixing and addition of surfactants, optimization of particle size, and slurry concentration (solid mass-to-slurry volume ratio).

3.1 *Optimization of parameters for sorption*

3.1.1 Effect of pH and chelating agent. One of the most important parameters for the quantitative sorption is the pH of sample. In order to improve the sorption

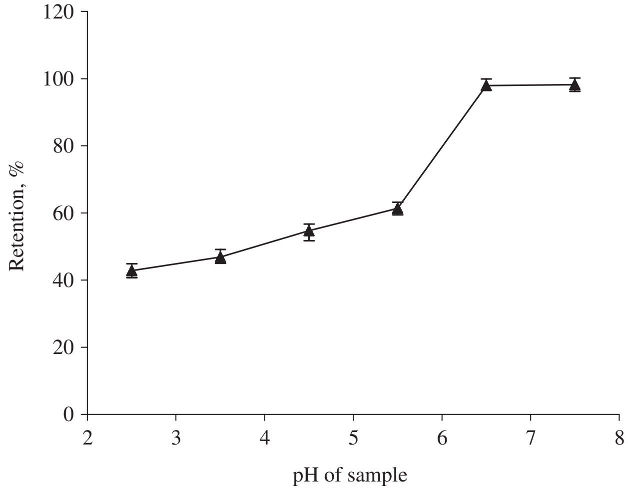

Figure 1. Effect of sample pH on sorption of cadmium with APDC (analyte concentration: 0.03 mg L^{-1}; sample volume: 40 mL; sorbent: 50 mg).

properties of a sorbent, it is mostly modified with a chelating agent. For this purpose, EGDMA-MA was treated with APDC as described in section 2. Although the sorption of 0.03 mg L^{-1} analyte on untreated EGDMA-MA was not successful, quantitative retention for the analyte cadmium was obtained upon modifying the sorbent with APDC. As can be seen from figure 1, when the pH of the solution was adjusted to $pH \geq 6.5$, the analyte could be quantitatively retained on the sorbent. It should be stated that the effect of pH was investigated using aqueous standards. However, since quantitative recoveries were obtained with sea water and bovine liver at the same pH as that of aqueous solution, we did not determine the effect of pH for every kind of sample. Obviously, the pH value for quantitative recovery of the analyte in aqueous solutions was valid for sea water and bovine samples.

3.1.2 Effect of amount of sorbent. In order to optimize the sorbent amount, the effect of different amounts of EGDMA-MA on the sorption of analyte was investigated. From a series of experiments, it was found that the analyte (0.03 mg L^{-1} Cd) was quantitatively sorbed using 50 mg of EGDMA-MA treated with APDC (figure 2). This value was also chosen as a critical parameter throughout the experimental works.

3.1.3 Effect of sample volume. The effect of sample volume on the sorption of analyte by 50 mg of EGDMA-MA treated with APDC was investigated up to 100 mL, and the results are given in figure 3. If the sample volume was less than 40 mL, quantitative sorption was obtained. For higher sample volumes, the amount of sorbent should be increased. Prolonged shaking time was not helpful in this matter. On the other hand, if the amount of sorbent is greater than 50 mg, a durable homogeneous suspension for slurry analysis could not be obtained using Triton X-100 and by stirring. In this case, a better mixing for homogenization with special tools is needed. Consequently, in all experiments, the sample volume did not exceed 40 mL.

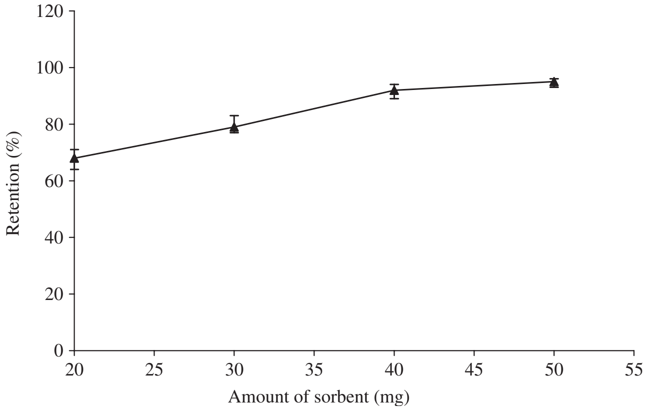

Figure 2. Effect of amount of sorbent (EGDMA-MA) on sorption of cadmium with APDC (analyte concentration: 0.03 mg L^{-1}; sample volume: 40 mL; pH: 6.5).

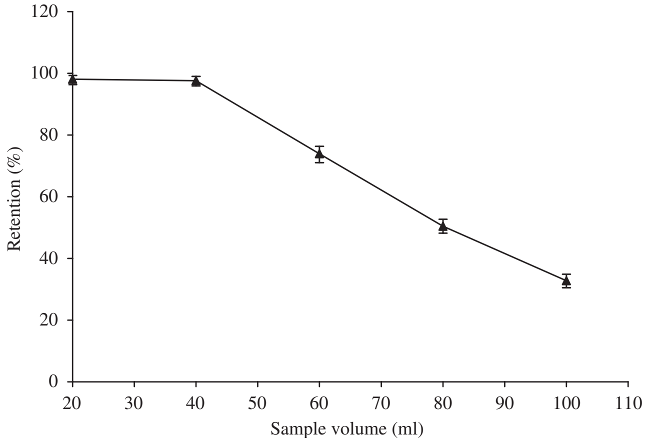

Figure 3. Effect of sample volume on the sorption of cadmium with APDC (analyte concentration: 0.03 mg L^{-1}; pH: 6.5; sorbent: 50 mg).

3.1.4 Effect of foreign ions. The effect of various foreign ions on the sorption of analyte was investigated. For this purpose, eight different chemical species were added to the test solution containing Cd, and the retention of analyte was found. The results are shown in table 2. Obviously, EGDMA-MA could be succesfully used for the determination of Cd in the presence of foreign ions at their concentrations given in the table. The concentrations of foreign ions are higher than those in most commonly studied samples with very heavy matrices, e.g. sea water, serum, etc.

3.2 *Effects of total slurry volume on homogenity of slurry*

The effects of total slurry volume on the analytical results were investigated, and the results in the presence of Triton X-100 are given in table 3. Since the sorbent could not

Table 2. Effect of foreign ions on the sorption of Cd[a].

Species	Added as	Concentration of the diverse ion (mg L^{-1})	Retention of Cd (%)
Na^+	NaCl	4800	110
	$NaNO_3$	400	99
	Na_2SO_4	1950	105
K^+	KCl	325	99
Mg^{2+}	$MgCl_2$	380	105
Ca^{2+}	$CaCl_2$	220	110
Fe^{3+}	$Fe(NO_3)_3$	35	99
Cu^{2+}	$CuSO_4$	25	110
Cl^-	NaCl	7200	110
	KCl	275	99
	$CaCl_2$	380	110
	$MgCl_2$	1120	105
NO_3^-	$NaNO_3$	1100	99
	$Fe(NO_3)_3$	115	99
SO_4^{2-}	Na_2SO_4	4050	105
	$CuSO_4$	35	110

[a] Analyte concentration: 0.03 mg L^{-1}; sorbent: 50 mg; sample volume: 40 mL; pH: 6.5; no. of replicates: 3.

Table 3. Effect of the total volume of the slurry (prepared in 1% of Triton X-100) on recovery of Cd[a].

Total slurry volume (μL)	Recovery of Cd (%)
200	39
400	98
600	94
800	61
1000	52

[a] Final analyte concentration: 0.03 mg L^{-1}; sorbent: 50 mg; sample volume: 40 mL; pH: 6.5; no. of replicates: 3.

be dispersed homogeneously and did not stay stable during in the absence of a dispersant, Triton X-100 was necessarily added as a dispersant in all solutions. As can be seen from table 3, when the slurry was prepared in 400 μL of 1% Triton X-100, quantitative recovery (98%) was obtained. By considering these results, all samples were prepared in 1% Triton X-100 as 400 μL. The low recovery percentage obtained for 200 μL of total slurry volume may be attributed to the fact that the amount of solid material (actually the ratio of solid amount to total slurry volume) was too high to be completely pipetted into the furnace as adjusted. The slurry had an almost mud-like quality and could not be pipetted (drawn and/or discharged) completely. On the other hand, at large slurry volumes, the homogeneity lasting during the whole analysis could not be maintained, and low precisions were obtained. As mentioned previously, when the sample and final slurry volumes were 40 mL and 400 μL, respectively, an enrichment factor of 100 was obtained. If higher concentration factors were used, the experimental factors for higher sample volumes and/or lower slurry volumes would need to have been altered, e.g. using special tools for a much effective mixing of slurry (ultrasonic blades, etc.), prolonged shaking time for quantitative sorption, higher concentrations of surfactants for the durability of a homogeneous slurry, etc.

In this study, the slurries were pipetted manually, which is actually not common in graphite furnace applications, whereas an autosampler is commonly used for delivering the sample drop precisely. Manual sampling into a graphite tube requires care, experience, and skill, so that the absorbances and peak shapes of repetitive pipettings for the same solution are always as good as those obtained using auto-samplers. This may be even more problematic with slurry injection. Therefore, the numerous slurry conditions were carefully optimized to obtain a homogenous and durable slurry as well as perfect and repetitive pipettings. After each injection, we controlled the position of the sample drop in the platform and observed its drying with a special mirror. In case of any problems during injection, the furnace programme was stopped, and the injection was repeated after thermally cleaning the tube. However, since the injections in previous studies were performed manually, the aforementioned problems were rare [17].

However, it should be noted that the simplicity of this method without the need for special tools is valid only in a limited range of experimental parameters given above and an enrichment factor of 100 was sufficient for the samples studied.

Almost no background value was observed, even if a low pyrolysis temperature was used without any matrix modifier, which indicates that the matrix was successfully separated, and the sorbent itself does not cause any significant spectral interference. Moreover, the addition of a mixture of 0.2 mg of $NH_4H_2PO_4$ and 0.01 mg of $Mg(NO_3)_2$ as a modifier barely improved the analytical data, and quantitative recoveries were obtained with and without modifier if samples, blanks, and standards were subjected to the same procedure. Nevertheless, all analyses were performed using the aforementioned modifier to prevent any risk of possible interference.

3.3 *Validation of the method*

To validate the method in different matrices, the cadmium was determined in sea water (CRM-SW) and bovine liver (CRM-BL) certified reference materials after suitable enrichment. The analytical results are given in table 4.

It should be noted that if quantifications for Cd were made after treating the samples, standards, and blanks in the same enrichment/separation method, the certified values were within the 95% confidence limits of certified values. Therefore, we applied a direct calibration method but not directly against matrix-free standards prepared from stock solution simply by dilution. Instead, for quantifications, samples, standards, and blanks were subjected to the same experimental procedure.

Table 4. Recoveries for Cd in sea water (CRM-SW) and bovine liver (CRM-BL) certified reference materials[a].

	Sea water ($\mu g\, kg^{-1}$)			Bovine liver ($\mu g\, L^{-1}$)		
Element	Certified value	Found[b]	Relative error	Certified value	Found[b]	Relative error
Cd	0.100	0.096 ± 0.004	−4.0%	3.0	2.9 ± 0.2	−3.3%

[a] Sorbent: 50 mg; sample volume: 40 mL; pH: 6.5; no. of replicates: 3; the slurry was prepared in 1% of Triton X-100.
[b] Mean ± 95% confidence limits.

The certified value of CRMs were within the 95% confidence limits of the mean values found as the average of three replicate independent determinations, which means that there are no significant differences between mean values of the analyte found as the average of three replicate independent determinations and their certified values in the 95% confidence level ($p > 0.05$). This obviously shows that after optimization of the experimental conditions, the analyte in different heavy matrices was quantitatively sorbed on EGDMA-MA treated with APDC, and the sorbent collecting the analyte was successfully analysed with slurry analysis. The calculated detection limit for cadmium using sample-matching blanks was $0.09\,\mu\text{g L}^{-1}$, according to the 3σ ($N = 10$) concept for the described method.

The method was validated by testing whether the certified values of CRMs (sea water or bovine liver) were within the 95% confidence limits of the mean values found from three replicate analyses of CRMs. The whole analytical procedure (including sorption and slurry preparation) was repeated three times using different aliquots of samples (sea water and bovine liver), and the results in table 4 were given as the averages (together with their confidence limits) of three successive measurements for the slurry of each sample aliquot used in the experimental procedure. Statistically, the higher the numbers of repetitions, the more reliable the resulting comparisons. Therefore, there is no definite number for replicates of analyses. However, in all articles, the number of replicates is three. This has been almost a standard value for the number of replicates. Therefore, we preferred three independent repetitions for a limited amount of CRM materials, and as for other articles, we made our repetitions three times, thus making a comparison of the precision of this method with those of other methods more realistic.

4. Conclusion

The method described in this study combines the advantages of batch enrichment/separation method and slurry analysis. Since the elution was not used, its drawbacks, such as incomplete elution, contamination, and loss of time, were eliminated. Therefore, the proposed technique is simple, fast, and cheap, and can yield high concentration factors of up to 100. Last but not least, better preconcentration factors can be achieved by adjusting the volume of the suspension, appropriately.

On the other hand, since the described method is a combination of sorption and slurry techniques, in the beginning, many experimental parameters had to be optimized for precise and quantitative sorption of analytes as well as in the preparation of homogeneous slurry and its reproducible pipetting. Despite the fact that various parameters need to be optimized, it can be concluded that the proposed technique can be used effectively and practically for the preconcentration and separation of cadmium prior to their determination by ETAAS.

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