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HAKAN DEMİRÖZ

OSMAN YAVUZ ATAMAN

NUSRET ERTAŞ

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Determination of cadmium in high salt content matrices by flow injection cold vapor atomic absorption spectrometry

Orkun ALP¹, Hakan DEMİRÖZ¹, Osman Yavuz ATAMAN², Nusret ERTAŞ^{1,*}

¹*Division of Analytical Chemistry, Faculty of Pharmacy, Gazi University,
06330 Ankara-TURKEY*

e-mail: nertas@gazi.edu.tr

²*Department of Chemistry, Middle East Technical University, 06531 Ankara-TURKEY*

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Flow injection cold vapor atomic absorption spectrometry (FI-CVAAS) was used for determination of cadmium in high salt matrices such as dialysis concentrates and textile leach solutions. The parameters such as acidity, concentration of reducing agent, reaction coil length, and carrier gas flow rate were investigated to obtain the best sensitivity. No significant background signal was observed even at high salt concentrations. Under the optimized conditions the limit of detection value ($3s_b m^{-1}$, where s_b is the standard deviation of the blank signals and m is the slope of the calibration graph) was found to be 0.05 ng mL^{-1} for an injection volume of $250 \mu\text{L}$ and the precision in terms of relative standard deviation was 3.2% using 11 consecutive measurements of 0.5 ng mL^{-1} standard. The standard addition method was used for quantitation. The accuracy of the method was tested using ETAAS as a comparison method and a certified reference material (Waste Water EU-L-1). In both cases, the results were in good agreement at 95% confidence level. The concentrations of cadmium in textile product leach solutions were found to be below the limit value assigned by Oeko-Tex standards.

Key Words: Cadmium, chemical vapor generation, dialysis concentrates, artificial sweat, textile leachates

Introduction

Trace and ultra-trace determination of cadmium in various samples continue to be a focus of interest due to its toxicity. Many sensitive and selective techniques have been developed for determination of cadmium at low levels,

*Corresponding author

including electrothermal atomic absorption spectrometry (ETAAS),^{1–5} inductively coupled plasma optical emission spectrometry (ICP-OES),^{6–9} and inductively coupled plasma mass spectrometry (ICP-MS).^{10–12} However, determination of cadmium at trace and ultra-trace levels in complex matrices, especially having high salt content, is not an easy task due to matrix related interferences. Determination of cadmium in the presence of high salt content is a current analytical problem for both plasma and ETAAS techniques. In plasma techniques, the non-spectral interferences caused by easily ionized major elements such as Na, K, and Ca result in enhancement or suppression of the signal in routine plasma conditions.^{13–18}

ETAAS has been used for trace metal determinations in several types of matrices because of its high sensitivity and capability of convenient ashing of sample during analysis. However, the major problem with ETAAS is the high salt content of urine, sea water, or sweat matrix, which produces high background signal and non-spectral interferences. Therefore, a separation and/or preconcentration step prior to atomic spectrometry analysis is often necessary. On-line column preconcentration techniques coupled with atomic spectrometry based on ion exchange,¹⁹ precipitation,²⁰ coprecipitation,^{21,22} solvent extraction,^{23–25} and solid sorbent extraction^{26,27} have been successfully applied for trace cadmium analysis. There are many studies about the interferences caused by chlorides of alkali and alkaline earth metals in graphite tube atomizers. When Pd is used with ammonium nitrate the interferences are eliminated up to 3 g L⁻¹ NaCl concentrations.²⁸ Welz et al.²⁹ have shown that when Pd-Mg is used as matrix modifier 0.5 g L⁻¹ NaCl can be tolerated for cadmium determination.

Chemical vapor generation (CVG) is considered an effective sample introduction technique with excellent matrix separation capability. Hydride generation (HG) is one of the most popular CVG methods, and it can be applied to the determination of elements (e.g., As, Sb, Bi, Ge, Sn, Pb, Se, Te) that form relatively stable and volatile hydrides.³⁰ Atomic absorption spectrometry can be coupled with CVG; it is one of the most sensitive techniques for the determination of cadmium at low levels. This technique offers several important advantages such as separation of the analyte from the matrix resulting in reducing the matrix related interferences and higher efficiency in sample introduction as compared with conventional nebulization. The advantages and drawbacks of using CVG-AAS and CVG-ETAAS for biological and environmental matrices have been reviewed by Tsalev.³¹ Cold vapor generation (CV) is another CVG method where the analyte is converted to atomic vapor at ambient temperatures; this method has been used for the determination of mercury and cadmium, employing detection by AAS. The sensitivity of the CVAAS system was found to be better than that of the heated quartz tube atomizer, since the residence time of the atomic cadmium species in the atomizer is less than that in the heated quartz tube atomizer due to thermal expansion.³² Vargas-Razo and Tyson³³ optimized the FI-CVAAS method for Cd determination. In their study, various gas-liquid separators and atom cell designs were investigated and the effects of some reagents such as cobalt, nickel, thiourea, and didodecyl-dimethylammonium bromide on sensitivity were studied in detail. Cadmium was determined in various matrices such as blood,³⁴ water,³⁵ sewage sludge,³⁶ human hair,³⁷ and soil³³ using flow injection cold vapor atomic absorption spectrometry (FI-CVAAS).

The textile industry is one of the main industry areas and the quality of textile products is important. Textile products contain various hazardous materials including heavy metals. Those heavy metals can either exist naturally in the structures of textiles or by sorption from the dyes used during production. The Oeko-Tex Standard 100 is a normative document published by Oeko-Tex and the limit values of heavy metals in textile

Reagents and solutions

Deionized (DI) water (18.2 M Ω .cm) obtained from a Milli-Q water purification system (Millipore, Milford) was used for the preparation of the solutions and all reagents were analytical reagent grade. The cadmium standard solutions were prepared by diluting the 1000 mg L⁻¹ (Fisher Scientific, UK) stock solution. Sodium borohydride $\geq 96\%$ (NaBH₄), hydrochloric acid (HCl), sodium hydroxide (NaOH), and magnesium nitrate (Mg(NO₃)₂) were purchased from Merck. NaBH₄ was used as reducing agent at the concentration of 3.0% (w v⁻¹) in 0.6% (w v⁻¹) NaOH (Merck). Mg(NO₃)₂ was used for coprecipitation of cadmium in the samples and as a matrix modifier for ETAAS measurements. *l*-Histidine monohydrochloride monohydrate (C₆H₉N₃O₂.H₂O), sodium chloride (NaCl), and sodium dihydrogen phosphate dihydrate (NaH₂PO₄.2H₂O) were used to prepare artificial sweat solution and were purchased from Sigma.

The concentrated dialysis samples contain 8%-40% (w v⁻¹) salt and the content of each sample is given in Table 1. Textile samples were made of cotton of different colors and obtained from the local markets; they were selected from the textile product class II. The products in class II are those worn with a large part of their surface in direct contact with the skin.³⁸

Table 1. The content of concentrated dialysis samples.

Content, g L ⁻¹							
	S1	S2	S3	S4	S5	S6	S7
NaCl	215.0	210.9	204.0	215.0	204.0	202.7	-
KCl	-	2.6	5.2	5.2	-	5.2	-
CaCl ₂ .2H ₂ O	9.0	6.4	9.0	9.0	9.0	9.0	-
MgCl ₂ .6H ₂ O	7.1	7.1	7.1	7.1	7.1	7.1	-
CH ₃ COONa.3H ₂ O	166.6	-	166.6	166.6	166.6	28.6	-
NaHCO ₃	-	-	-	-	-	-	84
CH ₃ COOH	-	6.3	-	-	-	4.2	-
Anhydrous dextrose	35	35	35	35	35	35	35

Sample preparation for FI-CVAAS and ETAAS methods

During the sample preparation of concentrated dialysis samples for the CV-AAS method the following procedure was used: an appropriate amount of concentrated dialysis sample (5-20 mL) was taken; concentrated HCl and DI water were added so that the final volume and final HCl concentration were 25 mL and 0.5 M, respectively. After dilution, the salt concentration of dialysis samples varied between 5% and 25 % (w v⁻¹) depending on the dilution ratio and type of the dialysis concentrate.

Artificial sweat solution was prepared according to ISO 105-E04 standard, as stated in the directions of Oeko-tex standards for textile products.³⁹ Artificial sweat solution contains 5.0 g of NaCl, 0.50 g of *l*-histidine monohydrochloride monohydrate, and 2.2 g of NaH₂PO₄.2H₂O per liter; the pH of the solution was adjusted to 5.5 with 0.10 M NaOH. The ratio between the textile product and the artificial sweat solution should be 1:50 (i.e. 1 g of textile product was treated with 50 mL of artificial sweat solution for the extraction) according to ISO 105-E04. Therefore, 1.0 g of textile product was extracted with 50 mL of artificial sweat solution for 30 min.

An appropriate amount of HCl was added to 8.0 mL of this extract in order to have a final HCl concentration of 0.5 M while the contents were diluted to 10 mL with DI water.

The textile leachate and concentrated dialysis samples cannot be analyzed directly with ETAAS due to the high salt content of the samples. Therefore, a sample pretreatment step should be applied before ETAAS measurements in order to eliminate the salt content of the matrix. Textile leachates and concentrated dialysis samples for cadmium determination were prepared as follows for ETAAS determination: 0.50 mL of $\text{Mg}(\text{NO}_3)_2$ (2000 mg L^{-1}) and 1.5 mL of NaOH (6.0 M) were added to 8.0 mL of both textile leachate and dialysis concentrate sample solutions. After waiting for 10 min, the solution was centrifuged at 3000 rpm for 30 min. Supernatant was removed and the precipitate was dissolved in 2.0 mL of 2.0 M HNO_3 ; the contents were then diluted to 10 mL with DI water.⁴⁰ The furnace temperature program used was as follows: drying step $10 \text{ }^\circ\text{C s}^{-1}$ ramp up to $120 \text{ }^\circ\text{C}$ and hold for 30 s, pyrolysis $50 \text{ }^\circ\text{C s}^{-1}$ ramp to $400 \text{ }^\circ\text{C}$ and hold for 20 s, atomization at $1200 \text{ }^\circ\text{C}$ for 3 s, and cleaning step at $2500 \text{ }^\circ\text{C}$ for 3 s. The standard additions technique was used for the ETAAS measurements.

Results and discussion

The HCl concentration in sample solutions (textile leachate and dialysis concentrates), carrier HCl, NaBH_4 concentrations, carrier gas flow rate, and reaction coil length are the parameters that directly affect the analytical signal in FI-CVAAS measurements. Therefore, these parameters were optimized by using aqueous cadmium standards and the optimum values for the FI-CVAAS method are given in Table 2.

Table 2. Optimized parameters for FI-CVAAS method.

Parameter	Value
Sample HCl concentration, M	0.50
Carrier HCl concentration, M	0.50
NaBH_4 concentration (w v^{-1}), %	3.0
NaOH concentration (w v^{-1}), %	0.60
Carrier gas flow rate, mL min^{-1}	230
Reaction coil length, cm	10

The sample HCl concentration is an important parameter to generate volatile cadmium species. Therefore, after evaluating the optimum HCl concentration by using aqueous standards, the acid concentrations of concentrated dialysis and textile samples were optimized in order to be sure that the composition of samples did not affect the analytical signal. With the exception of one concentrated dialysis sample (sample 7), the HCl concentrations of the samples were the same as those in the aqueous standards. The optimum HCl value for this dialysis sample shifted from 0.50 M to 0.75 M. The main difference in the content of this sample from the others is NaHCO_3 . The possible reason for this observation might be that NaHCO_3 reacts with HCl in the sample, depleting the acid and reducing its concentration. Thus, the optimum concentration (0.50 M) would not be sufficient to generate the cadmium vapor species. According to this observation 0.75 M HCl concentration was used while analyzing dialysis sample 7. The carrier HCl concentration was optimized in the range of 0.30-0.90

M. Up to 0.50 M HCl concentration, the signal increased slightly and after making a plateau the Cd signal started to decrease. Thus, 0.50 M was used as carrier HCl concentration throughout the experiments (Figure 2).

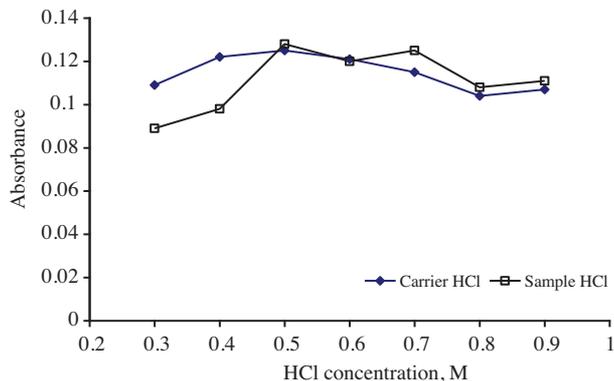


Figure 2. Optimization of carrier and sample HCl concentrations. Cd concentration was 2 ng mL^{-1} and the other parameters were kept constant as given in Table 2.

The concentration of NaBH_4 was studied in the range of 1.0%-5.0% w v^{-1} and the highest signal was observed at 3.0% w v^{-1} NaBH_4 concentration as shown in Figure 3. The concentration of NaOH in NaBH_4 solution also affected the signal and was studied in the range of 0.10%-1.0% w v^{-1} ; the maximum signal was obtained at 0.60% w v^{-1} (Figure 3). The flow rate of carrier gas was varied between 130 and 850 mL min^{-1} . The signal started to decrease when the carrier gas flow rate was increased. A 230 mL min^{-1} gas flow rate was selected considering the sensitivity and peak shape of the signal. The effect of carrier gas flow rate is shown in Figure 4. The length of the reaction coil was also studied in the range of 10-55 cm. It was found that the minimum coil length provides the highest signal as shown in Figure 4.

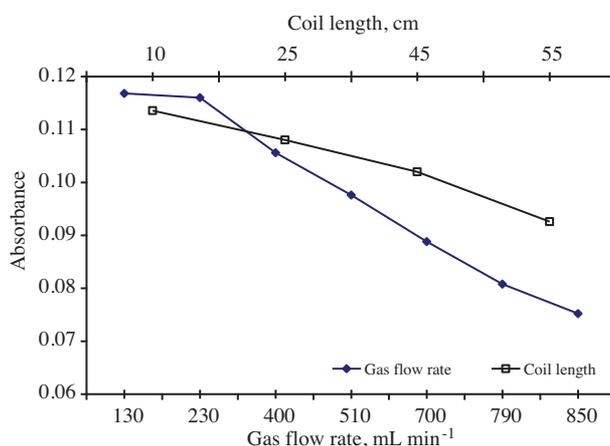
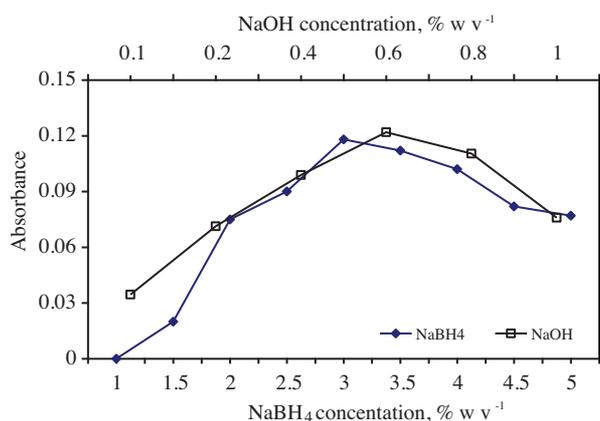


Figure 3. Optimization of NaBH_4 and NaOH concentrations. Cd concentration was 2 ng mL^{-1} and the other parameters were kept constant as given in Table 2.

Figure 4. Optimization of carrier gas flow rate and reaction coil length. Cd concentration was 2 ng mL^{-1} and the other parameters were kept constant as given in Table 2.

Analytical figures of merit

The limit of detection ($3s_b m^{-1}$, where s_b is the standard deviation of the blank signals and m is the slope of the calibration graph) of the proposed method was found to be 0.05 ng mL^{-1} and the linear range of the method was $0.5\text{-}6.0 \text{ ng mL}^{-1}$. The least squares regression analyses of the calibration curve for cadmium is $y = 0.0694 C_{Cd} + 0.025$ ($r^2 = 0.9995$), where y is absorbance and C_{Cd} is the concentration in ng mL^{-1} . The precision of the method in terms of RSD for 11 replicate measurements at 0.5 ng mL^{-1} level was found to be 3.2%. The sampling frequency was 100 measurements per hour.

The average absorbance value of blank solutions prepared for aqueous standards was around 0.008 A, where the absorbance value from reagent blanks (artificial sweat solution) was around 0.015. Although absorbance observed from the reagent blank is higher than that of the aqueous blank, it was not high enough to prevent quantitative analysis. The blank readings correspond to 0.12 ng mL^{-1} cadmium concentration when aqueous standard calibration is considered.

Accuracy of FI-CVAAS method

In order to validate the proposed method, Waste Water EU-L-1 (SCP-Science, Canada) certified reference material was used. The concentration of cadmium was found to be $60.7 \pm 1.8 \text{ ng mL}^{-1}$ ($n = 3$) while the certificate values after 1:100 dilution have been given as 0.06 mg L^{-1} and $0.058\text{-}0.062 \text{ mg L}^{-1}$ for the consensus value and confidence interval (95%), respectively. In addition, the accuracy of the proposed method was tested using ETAAS for comparison; the results will be discussed in the following section.

Determination of cadmium in samples

Although the matrix was separated during generation of volatile cadmium species, some of the matrix components still affected the cadmium signal. When the calibration curve slopes obtained with matrix matched standards were compared with the aqueous standards, differences were observed and the ratio of slopes of external to standard addition plots varied between 0.82 and 1.5. This observation could be interpreted as showing that each sample has its own effect on the signal. When the matrix was simulated as the dialysis samples, the slopes were not significantly different up to 5% ($w v^{-1}$) salt content as the matrix component. When salt content increased to 10% ($w v^{-1}$), the slope value was significantly different from the slope obtained with aqueous standards. For the spiked artificial sweat solutions, the slope value was not affected; however, when calibration was performed after extracting the textile products with the artificial sweat solution, the slope value was altered significantly. Therefore, the standard additions method was found to be necessary for accurate analysis of the samples. The results obtained with the proposed method are given in Table 3. The Oeko-Tex limit value for Class II textile products is 100 ng g^{-1} .³⁸ When this value was considered, cadmium concentrations in the textile samples used were found to be below the limit value.

After dilution of each sample, cadmium was spiked at a concentration of 2.0 ng mL^{-1} in order to validate the proposed FI-CVAAS method. The recovery values were between 90.6% and 111.7% (Table 4). ETAAS was used as a comparison method. The samples were analyzed by the ETAAS method after separation of the matrix by coprecipitation as $\text{Mg}(\text{OH})_2$ and the results are given in Table 3. FI-CVAAS results were in good agreement

with ETAAS results, using *t*-test at 95% confidence level. The detection limit of ETAAS method was 0.02 ng mL⁻¹ for 20 μL injection volume.

Table 3. Concentration of cadmium in dialysis concentrates and textile products obtained with FI-CVAAS and ETAAS.

Concentrated dialysis sample no.	Concentration, ng mL ⁻¹ (n = 3)		Textile product sample no.	^a Concentration, ng g ⁻¹ (n = 3)	
	FI-CVAAS	ETAAS		FI-CVAAS	ETAAS
1	2.15 ± 0.05	2.20 ± 0.04	1	8.8 ± 0.4	9.3 ± 0.6
2	3.28 ± 0.12	3.50 ± 0.17	2	7.4 ± 1.3	7.5 ± 0.5
3	1.93 ± 0.14	2.27 ± 0.10	3	10.7 ± 1.0	12.2 ± 0.8
4	1.52 ± 0.09	1.74 ± 0.17	4	< LOD	< LOD
5	1.81 ± 0.06	1.71 ± 0.05	5	15.61 ± 2.1	14.57 ± 1.3
6	2.05 ± 0.06	2.09 ± 0.17	6	< LOD	< LOD
7	0.49 ± 0.02	0.46 ± 0.01	7	< LOD	4.94 ± 1.7

^aConcentration refers to ng Cd leached for 1.0 g of the textile product.

Table 4. Recovery results of 2.0 ng mL⁻¹ spiked cadmium to the samples (n = 3).

Concentrated dialysis sample no.	Recovery, %	Textile products sample no.	Recovery, %
1	103.8 ± 1.6	1	109.8 ± 1.8
2	111.7 ± 1.2	2	103.8 ± 3.2
3	95.2 ± 2.1	3	109.5 ± 1.4
4	103.0 ± 5.6	4	100.5 ± 2.1
5	93.7 ± 5.4	5	101.0 ± 4.1
6	109.9 ± 5.5	6	101.8 ± 1.1
7	102.1 ± 0.8	7	90.6 ± 0.8

Conclusion

Determination of cadmium in high salt content matrices by FI-CVAAS technique offers distinct advantages in terms of interferences. Since no significant background signal was observed with sample solutions, direct analysis of the samples is possible without any need for sample pre-treatment. This is an important advantage when compared to ETAAS, where high background signals would be a problem in the presence of a high salt matrix. In addition, the proposed method is suitable for routine analysis since it is fast and simple; the low cost is another advantage when compared to other alternative methods such as ICP-MS or ETAAS.

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