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Comparison of Matrix Modifiers in the Determination of Cadmium and Lead in Industrial Waste Water Plants Around Cairo by Graphite Furnace Atomic Absorption Spectrophotometry

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The determination of lead and cadmium in waste water samples is of substantial importance for environmental monitoring, owing to their high toxicity and the possibility of human exposure to them (Purves, 1985). Lead is a very toxic because it attacks primarily the nervous system and accumulates in the form of protein-lead complex in the central nervous system (Fergusson, 1990). It inhibits a large number of enzymes having sulfhydryl functional group and thus interferes with cellular metabolism. Based on animal evidence, lead is regarded as a possible human carcinogen (Kendrick et al., 1992). Also, cadmium is considered as a toxic heavy metal because it attacks primarily the kidney and may produce lung cancer and also inhibits a large number of enzymes because it replaces zinc in enzymes and thus interferes with cellular metabolism (Cooke et al., 1990). It is found that the occurrence of certain cancer and cardiovascular diseases are related to the presence of trace pollutants such as cadmium. Also, it may substitute for calcium ions in the bone structure (Friberg et al., 1979). The US Environmental Protection Agency (USEPA, 1997) recommended a maximum permissible level of 0.05 $\mu g\ ml^{-1}$ for lead and 0.01 $\mu g\ ml^{-1}$ for cadmium in waste water.

Waste waters from mining industries activities, electroplating industries, paint industries or chemical laboratories contain very high concentrations of a wide variety of heavy metals, including the most toxic elements such as lead and cadmium. Release and dispersal of these toxic elements to aquatic systems can have disastrous consequences for living organisms. Therefore, monitoring of industrial effluents becomes increasingly important, particularly in highly industrialized areas.

In the analysis of sea and waste water samples for trace levels of lead and cadmium, a chemical preconcentration, such as solvent extraction, coprecipitation and ion-exchange, prior to graphite-furnace atomic absorption spectrophotometry (GFAAS) may be mandatory and serves the dual purpose of removal of the interfering major elements and increasing the concentrations of lead and cadmium (Liu et al., 1992 and 1993). These techniques besides being lengthy require ultrapure reagents. A simple, direct and more rapid method is desirable.

Direct graphite-furnace atomic absorption spectrophotometry analysis of water

samples has not proved to be reliable. This may be attributed to the problems of interferences due to the complex matrices encountered in environmental samples and to the relatively low atomization temperatures of Pb and Cd elements. Recent studies have indicated that the direct determination of Pb and Cd elements in various environmental samples in the presence of chemical modifiers, such as ascorbic acid (Bruhn et al., 1999), ruthenium (Silva et al., 1999 and Cai et al., 1997), hydrogen peroxide (Vinas et al., 1997), palladium (Locatelli et al., 1997), nitric acid (Zhou, 1996), magnesium nitrate Gottelet et al., 1996 and Miller, 1994), citric acid (Shan, 1987), oxalic acid (Kuan et al., 1999), sodium hydroxide (Lan, 1993), ammonium dihydrogen phosphate (Chuang et al., 1999 and Yu et al., 1996), thiourea (Ahsan et al., 1999), nickel nitrate (Tanaka et al., 1996), EDTA (Tsai et al., 1997 and White et al., 1998) and lanthanum-nitrate (Huang, 1995) by GFAAS, is a promising technique.

Since chemical and matrix effects are less severe in inductively coupled plasma atomic emission spectrometry (ICP-AES) than in graphite-furnace atomic absorption spectrophotometry (GFAAS) (Budic et al., 1994), ICP-AES has been widely used to determine Pb and Cd in various environmental samples (Uchida et al., 1993). The standard addition method should be used in ICP-AES in order to check the elimination of matrix interferences.

The aim of this work is to use some matrix modifiers such as ascorbic acid, EDTA, lanthanum nitrate, oxalic acid and citric acid in order to eliminate the effect of interferences due to the complex matrices encountered in industrial waste water samples around Cairo in the determination of Pb and Cd by GFAAS. These results are compared with those obtained by ICP-AES using the standard addition method and optimized conditions.

MATERIALS AND METHODS

All solutions were prepared from analytical reagent grade chemical. Stock solutions (1000 $\mu g\ ml^{-1}$) of Pb and Cd (all obtained from BDH) were diluted to provide working standards. All dilutions were performed with de-ionized water. Standard solutions of chemical modifiers such as ascorbic acid, citric acid, EDTA and lanthanum nitrate (1000 $\mu g\ ml^{-1}$) were prepared by dissolving 1 g of the dried substances (Fluka) in 1000 ml of de-ionized water obtained from Milli-Q water system.

The samples were filtered through membrane filters (Millipore, 0.45 mm), acidified with "ultra pure" trace – metal free nitric acid (0.5% v/v) and stored in polyethylene bottles. The polyethylene bottles were cleaned by soaking them in 5% v/v nitric acid overnight, followed by thoroughly washing with de-ionized water. The water samples studied were collected from different industrial plants around Cairo. Waste water samples, along with their replicates which were treated with 100 $\mu g\ ml^{-1}$ of different chemical modifiers, were analysed by direct injection of 20 µl volumes into the graphite tube by means of the auto-sampler. All the samples (or Standards) were subjected to the atomization programme presented in (Table 3).

Table 1. Instrumental parameters for graphite furnace atomic absorption spectrophotometry (GFAAS) for the determination of Pb and Cd elements

Parameter	Element	
	Pb	Cd
Wavelength (nm)	283.3	228.8
Slit width (nm)	0.7 low	0.7 low
Lamp type	Hollow cathode lamp	Hollow cathode lamp
Lamp current (mA)	8	20

Table 2. Operating conditions for inductively coupled plasma atomic emission spectrophotometry (ICP-AES)

Configuration	Scanning Czerny-Turner
Focal length	600 mm
Wavelength range	180-600 nm
Grating density	2400 lines/mm
Grating type	Holographic
Resolution	50,000
Generator	Crystal Controlled
Frequency	27.12 MHz
Operating power	1.4 KW
Argon coolant gas flow rate	20 L/min
Argon auxiliary gas flow rate	0.6 L/min
Sample uptake rate	1.5 ml/min

Table 3. Temperature programme for graphite furnace atomic absorption spectrophotometry (GFAAS) for the determination of Pb and Cd elements

Step	Pb			Cd		
	Temp °C	Ramp (S)	Hold (S)	Temp °C	Ramp (S)	Hold (S)
Drying	120	10	30	120	10	20
Ashing	500	10	20	400	10	20
Atomization	1100	0	5	1300	0	6
Clean-out	2650	1	5	2650	1	5

All laboratory wares were thoroughly cleaned by soaking in nitric acid (1:1 v/v) for at least, 24h. Immediately prior to use, all acid-washed wares were rinsed with de-ionized water.

A Perkin-Elmer model 5000 Atomic Absorption Spectrophotometer with Zeeman - background correction was used for this study. The spectrophotometer was equipped with an AS-50 auto-sampler and an HGA-500 graphite furnace. Hollow

cathode lamps and pyrolytic graphite coated graphite tubes were used. The instrumental parameters for GFAAS for determination of lead and cadmium are given in (Table 1). For each sample, ten replicate measurements were performed.

Analysis of the furnace gases was performed with a gas chromatograph (GC) model S 300 (Perkin-Elmer). The GC was fitted with a stainless-steel column, 2 in. long, 0.13 in. outside diameter, packed with 100 mesh carbosieve S-II and with a thermal conductivity detector. Gas samples were collected using a computerized sampling system. The gas sampling system was used to determine partial pressures of reducing gases (CO, H_2) produced by the pyrolysis of ascorbic acid or EDTA during the atomization temperature ramp of the furnace.

For the inductively coupled plasma atomic emission spectrometry analyses, a computer controlled ICP spectrometer model plasma S 135 (Kontron Co.) allowing automatic calibration and data acquisition was used. The ICP spectrometer was equipped with a sequential grating spectrometer of high resolution (Ca. 50,000) and a high - frequency generator which operates at 1.4 KW power and at working frequency of 27.12 MHz. Samples were nebulized with a rate of 1.5 ml/min with the use of a peristaltic pump. The analytical observation zone was 16 mm above the copper coil. The soft ware is written in Pascal and driven on an Apple IIe personal computer that controls the monochromator and processes the analytical data. For each sample, 10 replicate measurements were performed with an integration time of 10 Sec. Details of the instrument and optimum conditions are given in (Table 2).

RESULTS AND DISCUSSION

Direct determination of Pb and Cd elements in waste water samples by GFAAS is not feasible because of the problems of spectral, chemical and matrix interferences due to the complex matrices encountered in the samples. Spectral interferences may be eliminated by using Zeeman background-correction system. In our study the effect of the addition of a number of chemical modifiers, such as ascorbic acid, citric acid, EDTA, oxalic acid and La-nitrate was investigated. The results are summarised in (Table 4-5). Through the measurements, in order to improve the sensitivity, the concentration levels of various chemical modifiers were varied and optimized to be 100 $\mu g\ ml^{-1}$.

It is evident that the most effective of the chemical modifiers employed was ascorbic acid for Pb and EDTA for Cd (Tables 4-5). A substantial enhancement of absorbance was obtained for Pb and Cd in waste water samples in the presence of 100 $\mu g\ ml^{-1}$ of ascorbic acid and EDTA, respectively (Tables 4-5). Such enhancement may be explained by a gas-phase thermodynamic equilibrium model (Gilchrist et al., 1989).

The addition of such modifiers reduces the temperature of atomization of Pb and Cd to far below that of volatilization of other matrix components. This may be explained by reactions that occur between gaseous MO (M = Pb, Cd) and the

Table 4. Effect of addition of various chemical modifiers (100 μg ml^{-1}) on the determination of Pb in some waste water samples.

Waste water sample	Without reagents	Conc. Of Pb in μg ml^{-1} obtained by[a]					
		GFAAS					
		With ascorbic acid	With oxalic acid	With citric acid	With EDTA	With La-nitrate	ICP-AES[b]
Refining	121	411	382	351	302	251	402
Metallurgy	151	465	422	401	382	302	461
Ceramic Ind.	201	601	542	501	489	401	602
Plastic Ind.	82	305	251	202	201	149	301
Electronic Ind.	60	211	172	151	139	101	201
Textil Ind.	172	491	451	402	389	301	502
Paint Ind.	71	251	202	151	162	139	241

[a] All values given are the mean of ten replicate analyses, with relative standard deviations of 1-7%.
[b] Determined by the standard addition method

Table 5. Effect of addition of various chemical modifiers (100 μg ml^{-1}) on the determination of Cd in some waste water samples.

Waste water sample	Without reagents	Conc. Of Cd in μg ml^{-1} obtained by[a]					
		GFAAS					
		With ascorbic acid	With oxalic acid	With citric acid	With EDTA	With La-nitrate	ICP-AES[b]
Refining	31	51	40	61	122	35	113
Metallurgy	15	21	25	29	51	21	51
Ceramic Ind.	21	52	41	51	85	25	81
Plastic Ind.	8	20	15	21	30	10	30
Electronic Ind.	11	20	20	25	46	15	51
Textil Ind.	15	25	21	30	51	15	51
Paint Ind.	5	19	15	19	25	8	25

[a] All values given are the mean of ten replicate analyses, with relative standard deviations of 1-5%.
[b] Determined by the standard addition method

reducing gases formed by pyrolysis of the ascorbic acid or EDTA during the atomization temperature ramp (Gilchrist et al., 1990). The partial pressures of reducing gases (CO, H_2) produced by the pyrolysis of ascorbic acid or EDTA during the atomization temperature ramp are shown in (Table 6).

It is evident that the levels of H_2 and CO are below detection limits at the start of the atomization ramp and rise to a maximum at the end of the temperature ramp (Table 6). An indicated in Table 6, the levels of CO and H_2 produced from ascorbic acid or EDTA were much higher than those produced from nitric acid blank during atomization temperature ramp. It also shows (Table 6) that the levels of H_2 and CO produced by the pyrolysis of ascorbic acid or EDTA are

Table 6. Comparison of the partial pressures of H_2 and CO produced by the pyrolysis of ascorbic acid or EDTA and those from nitric acid blank during atomization temperature ramp.

Temp. (°C)	Modifier	Partial pressure x 10^4 (atm)	
		H_2	CO
800	ascorbic	ND	ND
	EDTA	ND	ND
	nitric	ND	ND
1000	ascorbic	60	30
	EDTA	50	30
	nitric	0.5	ND
1300	ascorbic	80	90
	EDTA	75	80
	nitric	15	20
1700	ascorbic	90	95
	EDTA	80	80
	nitric	90	90

ND : no detection

approximately the same as those from the nitric acid blank at the end of the temperature ramp. However, this is of little importance, since the lead and cadmium atomizations are complete at this point. It is evident that the levels of hydrogen and carbon monoxide do not affect the instrument background levels for lead or cadmium since these background levels in case of ascorbic acid or EDTA are approximately the same as those from nitric acid blank.

The concentration of the reducing gases and hence, the magnitude of atomization temperature shift are dependent on the type of chemical modifier used. The shift in the atomization temperatures of Pb and Cd is larger in presence of ascorbic acid and EDTA, respectively. This gas-phase mechanism is in line with that proposed by Bass et al., (1988) to explain the shift to higher atomization temperatures for Pb when atomized from an oxygenated graphite surface.

In order to check the success of the method, the samples were also analysed by ICP-atomic emission spectrometry (ICP-AES) using the standard addition method. In the determination of Pb and Cd elements by ICP-AES, the selection of instrumental parameters and optical wavelengths were based on obtaining good sensitivity, reasonable detection limits and eliminating interferences. The chosen analytical lines for the determination of Pb and Cd elements are 220.35 nm and 214.44 nm, respectively. Their detection limits are 4.0 $\mu g\ l^{-1}$ and 2.0 $\mu g\ l^{-1}$ for Pb and Cd, respectively. The results obtained for ICP-AES measurements using standard addition method are also summarized in (Tables 4-5).

A satisfactory agreement was achieved by comparing the results obtained by ICP-AES using standard addition method and GFAAS using ascorbic acid and EDTA

of Pb and Cd, respectively, in waste water samples. The accuracy of the method was investigated by determining the recovery of the spiked analyte to the waste water samples. A good correlation was obtained between analyte added and found. Significantly high recoveries were obtained for Pb and Cd when spiked in waste water samples (96-102%). The relative standard deviations (n = 10) were found to be 1-7% for Pb and 1-5% for Cd (Tables 4-5).

Least squares statistical data between the values measured for Pb and Cd by the proposed method and that measured by ICP-AES using standard addition method (Tables 4-5) gave a slope value close to 1 and a correlation coefficient higher than 0.999. Sensitivities, defined as the slopes of the calibration graphs are 0.01 and 0.05 for Pb and Cd, respectively. Detection limit was calculated as three times the standard deviation for ten consecutive measurements of the signal from a reagent blank and was found to be 2.0 and 1.0 $\mu g\ l^{-1}$ for Pb and Cd, respectively.

So, direct determination of Pb and Cd in waste water samples by GFAAS is not fessible because of the nature and complexity of matrices encountered in environmental samples. The addition of chemical modifiers, such as ascorbic acid and EDTA to waste water samples allows the direct determination of Pb and Cd, respectively, by GFAAS. The effects of addition of ascorbic acid and EDTA on Pb and Cd signals, respectively, are explained by a gas-phase mechanism.

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