STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LII, 2, 2007

DETERMINATION OF CADMIUM IN ENVIRONMENTAL SAMPLES USING THE METHANE - AIR FLAME ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT. The cadmium content of some soil, tree leave, grape and lichens samples has been determined directly by flame atomic absorption spectrometry using the methane-air flame. The flame and instrumental parameters were optimized; the best results were obtained with the lamp current of 5 mA, at the observation height of 11 mm, with the stoichiometric flame. The detection limit of 0.05 ± 0.02 mg.L^{-1} was obtained at a significance level of 0.05. The cadmium content of environmental samples has been determined with the external calibration curve and the standard addition method. In all cases, the results of two methods agree within the quantification error.

INTRODUCTION

Cadmium is relatively rare element; its abundance in the lithosphere is estimated at about 0.5 mg.kg^{-1} in the earth's crust. Due its several attractive physical and chemical properties cadmium is largely used in the industry. The major use of cadmium is for plating, mainly iron and steel articles, to form a protective coating. Cadmium is used in many alloys too, such as bearing metals, solders, electrical conductor, fusible metals and jewelry. The main sources of cadmium pollution are the ferrous metal and steel production, industrial Cd applications and nonferrous metals mining and production. Cadmium lands on environment via air deposition, sludge application and, in unusual conditions, via liquid effluents and solid wastes from Cd-processing plants. It can enter the human body mainly via drinking water, plants and animal food products, respectively. The quantity of cadmium in these products is proportional to the cadmium loading of the environment (natural water and soil especially) [1-3]. Cadmium has no physiological importance but it is considered as one of the most poisonous heavy metal for all living

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organisms. In the plants, among other effects, inhibits the photosynthesis, the activity of some enzyme activity, as H+-ATPase etc.[4-7]. Entering the animal or human organism by ingestion cadmium causes immediate poisoning and irreversible damage to the liver and the kidneys [8,9]. As calcium, magnesium and zinc antagonist chronic cadmium poisoning can leads to osteomalacia and osteoporosis in humans, called the Itai-Itai disease (occurred first in Japan in 1912, latest in '70-es) [10]. Cadmium can produce sterility, exhibits carcinogenic and teratogenic effects too. Therefore, accurate and reliable control of the whole cadmium content in different samples is required.

Flame atomic absorption spectrometry (FAAS) is probably the most widespread analytical method for the determination of cadmium in low concentrations. Usually the high temperature C_2H_2-air, C_2H_2–N_2O flames are used as atomization source, the detection limit of the cadmium by direct aspiration being of order of 10^{-3} -10^{-4} mg.L^{-1} [11, 12]. Cadmium is present usually in trace levels in the environment, in some cases the analyte had to be concentrated prior the quantification, as by: on-line sorption [13]; solid phase extraction on different adsorbents such as: Amberlite XAD-2010 resin [14]; Amberlite XAD-2 resin loaded with TAM reagent [15]; cellulose nitrate membrane filter [16]; bonded silica gel [17-20].

The low temperature (~ 2000 K) propane-butane-air (PB-A) flame was used in few cases for the determination of cadmium, mostly in early stage of the flame atomic absorption spectrometry development. The methane-air (M-A) flame has similar properties (temperature, burning velocity etc) with the PB-A flame [21]. To our best knowledge the behaviour of cadmium in the M-A flame was not studied, and the detection limits are not known.

The aim of the present work is to optimize the flame and the instrumental parameters for the AAS determination of Cd in the M-A flame, to apply the results for quantification of Cd in different environmental samples by direct aspiration without sample concentration prior analysis.

EXPERIMENTAL

INSTRUMENTATION

The measurements were carried out at 228.1 nm with a single beam HEATH-701 (Heath Co., Benton Harbor, MI, USA) spectrometer. A cadmium hollow-cathode lamp was used (NARVA, Germany), in connection with a HEATH EU-700 scanning monochromator, a HEATH EU-700-30 type photomultiplier module and a 1P28A (RCA, USA) photomultiplier (-360 V). The photomultiplier signal was introduced via a home made I/U and A/D converter (National Instruments) into a Pentium 2 PC and processed using in Quick Basic language written software. The data acquisition speed was of 100 ms, one recorded data represents the mean value of 50 measuring points, each point being the average of 300 individual measurements. The pneumatic nebulizer-spray chamber-burner system was used from an AAS-1 (Carl Zeiss Jena) atomic absorption spectrometer. The original slot type burner-head (for C_2H_2-air flame) was replaced with a similar, Mecker type, developed by us for atomic absorption measurements in the M-A flame [22]. The air flow-rate was kept constant, 500 L/h, the flow rate of the methane being varied as a function of the gas mixture wanted. As CH_4 source the city gas of 99 % purity was used, from the pipe.

CHEMICALS

The cadmium stock standard solution (1000 $mg.L^{-1}$) was prepared by dissolving in HCl (analytical grade, Merck, Darmstadt, Germany) of 1 g of metal (Specpure, Johson Matthey Chemicals Limited, England). The diluted standards were prepared by dilution with double distilled water.

SAMPLING AND HANDLING

The top soils were collected in 5-10 cm depth, the vegetal organic matter was removed (roots, leaves, boughs etc.), dried in oven at 105 °C, grinded and sieved. 2 grams of samples were taken for analyses. The samples were treated with 10 mL of concentrated HCl and heated carefully on hot plate for 30 minutes. Then 1 mL of concentrated HNO_3 was added and heated for further 5 minutes, and filtered. The clear filtrate was completed to a volume of 50 mL. The tree leaves (*Juglans regia, Prunus domestica, Vitis vinifera)* were collected in July after two weeks of dry season. The leaves were dried first at room temperature than in the drying oven at 90 °C. Lichen samples (*Xantoria parietina*) were collected from the cortex of trees by cutting with a sharp knife. After removal the rest of cortex, the lichens were dried in oven at 90 °C. The dry samples were finely grinded, about 2 g were taken for analysis. The samples were digested by treating with 10 mL of concentrated HNO_3, allowed to stand overnight, and heated carefully on hot plate until the production of red NO_2 fumes ceased. After cooling 2 mL of 70% $HClO_4$ were added and heated again to allow evaporating to a small volume. Finally, the clear digests were diluted to a volume of 50-mL with distilled water. The grapes sap was collected in springtime during the pruning. The clear liquid drops were collected directly into the 5 mL vials and were kept in the refrigerator at 4 °C until analysis. The saps samples were used directly, without any treatment.

PROCEDURE

The behaviour of cadmium in the M-A flame was observed in the flame up to h = 16 mm over the burner head (in 1mm steps). Three different flame compositions were used: 0.88; 1.00 and 1.12, expressed in relative stoichiometric units (RSU). Four replicate measurements were made in each case. The mean, the standard deviation, the S/N was calculated for each h and flame composition investigated. The homogeneity of the means was tested by the F test at a significance level of 0.05. The spectral bandpass of the monochromator was of 0.1 nm (width of the slit of 0.050 mm).

RESULTS AND DISCUSSION

OPTIMIZATION OF THE FLAME AND INSTRUMENTAL PARAMETERS

First, the hollow-cathode lamp current was optimized, by measuring the absorption (A) of the calibration solution of 1 mg.L^{-1} Cd at different lamp current intensities (i), between 2 – 10 mA, in 1 mA steps. The composition of the flame was constant, of 1.12 RSU, the observation height over the burner (h) was of 9 mm. The results are summarized in the Table I.

Table I.

The i - A relationship for 1 mg.L^{-1} of Cd in the M-A flame

i (mA)	A	S/N ratio	RSD (%)
2	0.063	2.24	11.1
3	0.058	6.80	6.9
4	0.056	7.22	7.1
5	0.058	12.60	5.2
6	0.055	10.17	3.6
7	0.048	7.86	4.2
8	0.044	12.00	4.5
9	0.043	5.78	4.7
10	0.044	8.33	4.5

The absorption of cadmium is maximal at i = 2 mA and decreases non-uniformly with the increase of the lamp current. The A – i relationship could be described best with a sixth order polynomial function. The curve presents a slow increase in the i = 4 – 6 mA range with the local maximum at the i = 5 mA. At this lamp current value the S/N ratio of the determinations is also maximal, of 12.6 (RSD = 3.44%). We can consider that the optimal value of the lamp current for the determination of cadmium is of 5 mA.

Further, the influence of the flame composition and that of the observation height on the absorption of cadmium was investigated. Three flame compositions (0.88, 1.00, 1.12 RSU) were used, the concentration of the analyte was 1 mg.L^{-1}. The lamp current was the optimal one. The absorption data versus observation height and flame composition are presented in the Fig. 2.

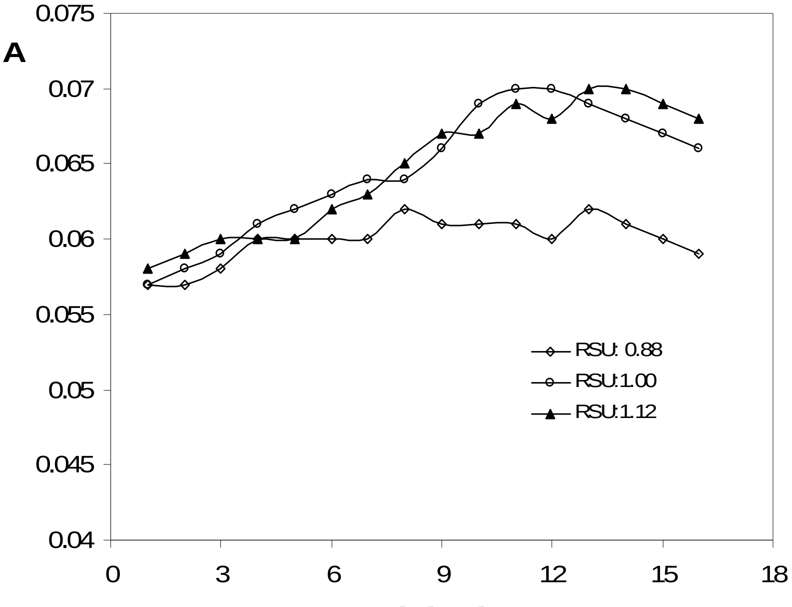

Figure 2. The variation of the absorption of the 1 mg.L^{-1} cadmium vs. observation height and flame composition.

The analytical signal depends both on observation height and flame composition. The absorption increases slowly with the increase of the methane content of the flame, being the highest in stoichiometric gas mixture (1.00 RSU). The highest absorption was observed at the same height of 11 mm over the burner, regardless of flame composition. The standard deviation of all means was homogeneous, the magnitude of the S/N ratio being decided by the magnitude of the mean. In conclusion, the optimal conditions for the quantitative determination of cadmium in the M-A flame are h = 11 mm and flame composition of 1.00 RSU.

CALIBRATION, DETERMINATION OF THE DETECTION LIMIT

For the determination of the detection limit the variation of the analytical signal versus concentration was studied in the 0.01 – 50 $mg.L^{-1}$ cadmium concentration range. Three calibration curves were plotted. Each calibration curve was established by using six standard solutions. Six replicate measurements were made at each concentration level. The homogeneity of the means and the linearity of the calibration curve were tested. The equation of the regression line, the confidence limits and the coefficient of correlation (R) were calculated with the least squares method. The detection limit was calculated for the fixed values of (P10)0 = 0.025 and (P11)d = 0.975. The results are summarized in Table II.

Table II

Calibration data of cadmium determination in the M-A flame

No. Eq.	Concentration range ($mg.L^{-1}$)	Equation of the calibration curve	Detection limit ($mg.L^{-1}$)
1.	0.1 – 2	$A = 0.064 * C - 0.0035$ $R = 0.9998$	0.05 ± 0.02
2.	2 – 10	$A = 0.0417 * C + 0.0669$ $R = 0.9934$	0.77 ± 0.36
3.	0.1 – 50	$A = 0.00001 * C^3 - 0.0015 * C^2 + 0.0627 * C +$ $+ 0.0012$ $R = 0.9997$	not calculated

The A – C relationship is not linear in the whole concentration range. The best fitted linear relationship was found in the 0.1 – 2 $mg.L^{-1}$ domain, the detection limit was of 0.05 ± 0.02 $mg.L^{-1}$. This value is low, but about two orders of magnitude higher than those obtained in the acetylene flames. In the 2 – 10 $mg.L^{-1}$ domain the A – C relationship is still linear, the detection limit being of same order of magnitude with that obtained earlier. Beyond 10 $mg.L^{-1}$ the calibration curve bents progressively toward the abscissa, exhibiting the well known saturation phenomenon. The A-C relationship for the entire 0.1 – 50 $mg.L^{-1}$ concentration range can be approximated best with a third order polynomial curve.

DETERMINATION OF CADMIUM IN THE ENVIRONMENTAL SAMPLES

The cadmium content of the samples was determined both by the calibration and by the standard addition method. The later method was used in order to study the presence of possible interference and/or as reference method due to the absence of certified reference material. The determinations were carried out with optimized flame and instrumental parameters. Four parallel measurements were made in each case. The measuring sample solutions were prepared in 25 ml volumetric flasks. In the case of standard addition method 50 µl of concentrated cadmium standard of 100 mg.L^{-1} was added to the 1 mL of diluted sample. Three additions of standard were made, in 0.5 mg.L^{-1} concentration steps. It was calculated the regression line, the cadmium content was determined from the intercept with the abscissa of the line. The results of the determination of cadmium content of the environmental samples are summarized in the Table III.

Table III

Results of analysis of the environmental samples (n = 4)

Sample		Concentration (mg.kg^{-1}, by standard calibration)	Concentration (mg.kg^{-1}, by standard addition)
Soil	Nr. 1	4.9 ± 0.3	5.4 ± 0.2
	Nr. 2	4.6 ± 0.3	5.1 ± 0.3
	Nr. 3	7.4 ± 0.3	8.3 ± 0.3
	Nr. 4	4.0 ± 0.3	4.3 ± 0.2
	Nr. 5	3.0 ± 0.3	3.1 ± 0.2
	Nr. 6	2.9 ± 0.3	3.1 ± 0.2
Lichen	Nr. 1	n.d.	0.5 ± 0.3
	Nr. 2	1.3 ± 0.3	1.5 ± 0.3
	Nr. 3	n.d.	2.0 ± 0.3
	Nr. 4	n.d.	0.3 ± 0.3
	Nr. 5	1.6 ± 0.3	1.8 ± 0.3
	Nr. 6	n.d.	1.3 ± 0.3

Grape sap	Nr. 1	n.d.	0.5 ± 0.3
	Nr. 2	1.4 ± 0.3	1.3 ± 0.3
	Nr. 3	n.d.	1.8 ± 0.3
	Nr. 4	1.3 ± 0.3	1.5 ± 0.3
	Nr. 5	n.d.	1.5 ± 0.3
	Nr. 6	2.4 ± 0.3	2.0 ± 0.3
Tree leaves	Nr. 1	n.d.	0.8 ± 0.3
	Nr. 2	n.d.	1.0 ± 0.3
	Nr. 3	2.8 ± 0.3	3.3 ± 0.3
	Nr. 4	n.d.	1.3 ± 0.3
	Nr. 5	n.d.	2.0 ± 0.3
	Nr. 6	2.0 ± 0.3	2.5 ± 0.3

The results of the two methods are very close, they usually agree within the errors of the determinations. In some cases it was impossible to separate unambiguously the analytical signal from the background (noted n.d.). In all these cases the quantification of the cadmium was possible only by the standard addition method.

In conclusion the methane-air flame allows the direct determination of cadmium in low concentrations without prior concentration of the analyte. The close results show the lack of interferences in the M-A flame, as observed in the acetylene flames. We consider, that for higher cadmium concentrations the standard calibration method is recommended, for concentrations close to the detection limits the standard addition method offer better results, closer to the real cadmium content of the samples. As final conclusion cadmium can be quantified precisely in soil and vegetal samples by direct aspiration using the M-A flame, without prior concentration of the analyte.

CONCLUSIONS

In the M-A flame cadmium exhibits a strong absorption of the resonance line, at the 228.8 nm. The absorption varies with the hollow-cathode lamp current, with the composition of the flame and observation height. The optimal lamp current is of 5 mA, the of observation height over the burner head is 11 mm, in stoichiometric flame (RSU = 1.00). The absorption-concentration relationship is linear in the 0.1-10 mg.L^{-1} range, the detection limit is of 0.05 ± 0.02 mg.L^{-1} of cadmium. The cadmium content of soil, lichen, tree leave and grape sap samples can be determined accurately using the external calibration or the standard addition method. In conclusion, M-A flame is a suitable for precise atomic absorption determination of cadmium in different environmental samples.

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