

Study of the Versatility of a Graphite Furnace Atomic Absorption Spectrometric Method for the Determination of Cadmium in the Environmental Field

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Cadmium is a representative example of trace elements that are insidious and widespread health hazards. In contemporary environmental analysis, there is a clear trend toward its determination over a wide range of concentrations in complex matrixes. This paper describes a versatile method for the determination of Cd at various levels (0.1–500 µg/g) in several sample types, such as soils, sediments, coals, ashes, sewage sludges, animal tissues, and plants, by graphite furnace atomic absorption spectrometry with Zeeman background correction. The effect of the individual presence of about 50 elements, with an interference/analyte concentration ratio of up to 10⁵, was tested; recoveries of Cd ranged from 93 to 106%. The influence of different media, such as HNO₃, HCl, HF, H₂SO₄, HClO₄, acetic acid, hydroxylammonium chloride, and ammonium acetate, in several concentrations, was also tested. From these studies it can be concluded that the analytical procedure is scarcely matrix dependent, and the results obtained for a wide diversity of reference materials are in good agreement with the certified values.

Because heavy metals are vital components in the development of modern technology, their levels dispersed in the environment have increased at a rate that has been greatly accelerated during the 20th century.

Absorbed in sufficiently high amounts, heavy metals can be toxic and even lethal. In particular, the toxicity of cadmium (Cd) to plants, animals, and human life is well documented in several studies (1–7). Cd is an insidious and widespread health hazard at trace levels. When inhaled, it is completely absorbed through the lungs, and it is known to induce arterial hypertension and affect the kidneys (8).

Today, the challenge facing the scientific community and regulatory agencies is to assess the health risks of low-level exposure to heavy metals in the environment. Accordingly, new analytical procedures enabling the determination of trace and ultratrace levels of analytes are needed. In particular, in contemporary environmental analysis there is a clear trend toward the determination of Cd at the lowest possible levels in complex matrixes.

In 1999, Rucandio and Petit (9) described a new method for the determination of Cd by graphite furnace atomic absorption spectrometry (GFAAS). Among several types of matrix modifier tested, a mixture of 2% (w/v) NH₄H₂PO₄ and 0.4% (w/v) Mg(NO₃)₂ in 0.5M HNO₃ was selected, because it provided the highest sensitivity. With this modifier, several conditions (ashing and atomization temperatures, heating rate, use of L'Vov platform, etc.) were optimized. Concentration results obtained by using the standard additions method and direct analysis showed good agreement. The latter is preferred because it is the simpler and less time-consuming method, providing a detection limit of 0.13 µg/L with measurement of peak areas. In the present work, our aim was to extend the applicability of the method to allow the determination of a wide range of Cd concentrations in a series of representative environmental matrixes. Consequently, we studied the effect of other minor or major elements that could be present in these types of samples, as well as the influence of different media.

Experimental

Chemicals and Reagents

All reagents used were analytical reagent grade or Suprapur and were obtained from Merck (Darmstadt, Germany).

(a) *Ultrapure water*.—Used throughout.

(b) *Certified stock solution of Cd containing 1000 mg/L*.—Johnson Matthey GmbH Alpha (Karlsruhe, Germany), Specpure. Used to prepare the rest of the Cd solutions by dilution with 0.5M HNO₃.

Components of solutions of the other elements used in this work are listed in Table 1; the elements were highly pure and free of Cd content.

(c) *A mixture of 2% (w/v) NH₄H₂PO₄ and 0.4% (w/v) Mg(NO₃)₂ in 0.5M HNO₃*.—Used as a matrix modifier.

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Table 1. Elements considered in the interference study

Medium	Element
HNO ₃ , 5%	Ag, As, Ba, Be, Bi, Ca, Ce, Co, Cs, Cu, Fe, Ga ^a , Ge ^a , Hg, In, K, Li, Mg, Mo ^a , Na, Ni, Pb, Rb, Sc, Se, Si ^a , Sr, Tl, Ti ^b , V, W ^b , Y, Zn
HCl, 20%	Ir, Os, Pt, Rh, Sb, Sn, Te, Pd
HCl, 5%	Al, Cr(III), Hf, Zr
HF, 2%	Nb, Ta
Aqua regia, 5%	Au
NH ₄ OH, 1%	B

^a Plus trace amounts of HCl.

^b Plus trace amounts of HF.

All standards and reagent solutions were stored in polyethylene containers; glassware and polyethylene materials in contact with samples or reagents were cleaned with 4M HNO₃ overnight and rinsed with ultrapure water.

Apparatus

(a) *Microwave oven*.—CEM MDS 2000; used for digestion of samples.

(b) *Spectrometer*.—Used to make all atomic absorption measurements; Varian (Mulgrave, Victoria, Australia) SpectrAA-640Z fitted with a transverse Zeeman effect background corrector and equipped with a Varian PSD-100 sample dispenser.

(c) *Graphite tube atomizer*.—Used to perform electrothermal heating of the samples; Varian GTA-100.

(d) *Pyrolytic graphite tubes*.—Varian P/N 63-100023-00.

(e) *Pyrolytic forked platforms*.—Varian P/N 63-100024-00.

Dissolution Procedure

For Cd determination, all environmental samples were treated as follows: 5 mL ultrapure water + 7.5 mL concentrated HCl + 2.5 mL concentrated HNO₃ + 4 mL concentrated HF were added to 250 mg sample. The mixture was subjected to the previously established microwave oven program (9), using closed vessels. Finally, all solutions were filtered and diluted to 50 mL with ultrapure water in polypropylene flasks.

Determination of Cd

Samples were analyzed without any other treatment, except dilution to suitable volume with 0.5M HNO₃ in the case of high Cd content. When small dilutions are required, the instrument is able to take a lower sample volume and to calculate the concentration, taking into account the corresponding dilution.

Analytical conditions were previously optimized (9) and are summarized with some improvements as follows: wavelength, 228.8 nm; measurement mode, area; type of background correction, Zeeman effect; slit width, 0.5 nm; slit height, reduced; matrix modifier, 2% (w/v) NH₄H₂PO₄ + 0.4% (w/v) Mg(NO₃)₂ in 0.5M HNO₃; modifier volume, 5 L; sample volume, 10 L; total volume, 25 L; drying/ashing/atomization/clean-

ing temperatures, 95/900/1900/2500 C; calibration range, 0.5–10.0 g/L; and calibration algorithm, quadratic origin.

Results and Discussion

The final purpose of this work was to ascertain whether the proposed method has general feasibility for the determination of a wide range of Cd concentrations in a broad variety of matrixes, such as soils, sediments, sludges, ashes, coals, and biological materials (animals and plants). To fulfill this goal, it was necessary to study the effects of other minor or major elements potentially present in these environmental samples, as well as the influence of different reagents commonly used in dissolution procedures.

Influence of Other Elements

Because standard solutions of Cd were prepared in 0.5M HNO₃ without concomitants, it was necessary to test whether other elements would produce a positive or negative effect in the determination of trace levels of Cd. For this purpose, individual solutions containing concentrations of each possible interfering element at 500 mg/L and of Cd at 5 g/L (in the middle of the calibration curve) were prepared. Recoveries of Cd added were calculated from the concentrations found in the presence of each element. The average recovery for 10 assays of Cd standard solution was 100.0 ± 1.8%. Figure 1 shows these average Cd recoveries for 10 measurements in the presence of each concomitant element. The error bars represent the uncertainties of the measurements for a confidence level of 95%. Good recoveries were obtained in the presence of each of the possible interfering elements, ranging from 93 to 106%, with an average relative standard deviation (RSD) of 2.4%; all RSDs were < 7%. These very satisfactory results showed minimal differences between standard solutions of Cd and solutions containing both Cd and another element, even though the interference/analyte concentration ratio was equal to 10⁵. Thus, there was no remarkable effect because of the presence of any of the elements tested.

The uncertainty obtained in the case of boron was significantly higher than those obtained for the other elements. These fluctuations can be attributed to very high background levels that were already reported in a previous paper (9), when the samples were treated with boric acid after digestion.

Recoveries of Cd ranging from 93 to 95% were obtained in the presence of Ir, Os, Rh, Ti, and W. None of these elements are normally present in environmental matrixes at high concentrations. Consequently, these results will not have a significant influence on the determination of Cd. Be and Sn gave rise to Cd recoveries of about 106%. These high recoveries could be due to very small Cd impurities in the solutions of these elements.

On the other hand, there are also significant statistical differences, at a confidence level of 95%, in the recoveries obtained for Cd in the presence of Cr, Li, Mg, Na, Nb, Sb, Ta, V, and Zn (95–98%) and Al, Ba, Ca, Cs, Ga, and K (103–105%). Nevertheless, these results can be considered satisfactory. In the case of Al, Ca, Na, and Mg, present as major constituents in certain environmental samples, the as-

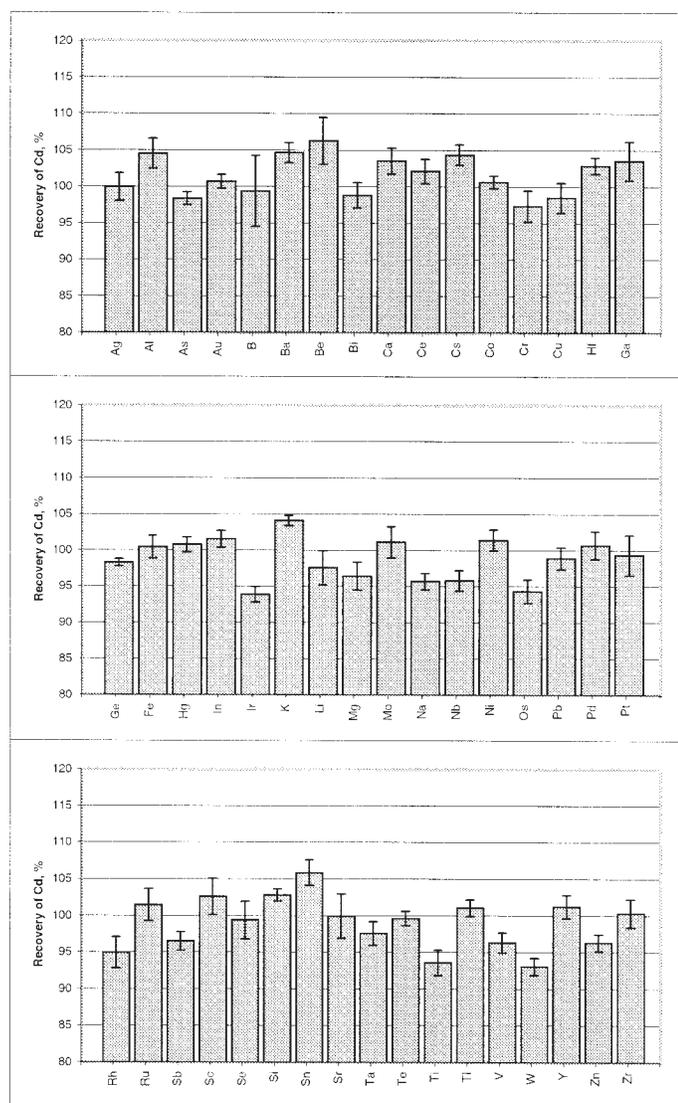


Figure 1. Recovery (%) of Cd in the presence of various elements. The interference/analyte concentration ratio was equal to 10^5 . Error bars are 95% confidence intervals of 10 independent analyses, calculated as ts/\sqrt{n} where the t -statistic = 2.262 for 9 degrees of freedom.

says were repeated with an interference/analyte concentration ratio equal to 10^6 , with recoveries of 99, 102, 95, and 97%, respectively. These results show the absence of influence by these elements.

Evaluation of Different Media

To extend the applicability of this method to samples dissolved by another procedure, we explored the effects of type and concentration of acid on the resultant Cd signals. Therefore, several individual inorganic acids (HNO_3 , HCl , HF , H_2SO_4 , and HClO_4), an acid mixture, i.e., aqua regia (HCl-HNO_3 , 3 + 1), and a single organic acid (CH_3COOH) were tested. (*Warning: HClO_4 is extremely hazardous. Its use can cause a fire or explosion resulting in death or injury. Never use this acid in the graphite furnace with organic samples.*)

These acids could lead to the formation of unexpected species of Cd and of other matrix constituents that might affect the determination of Cd. Consequently, solutions containing Cd at 5 $\mu\text{g/L}$ in each acid type at different concentration levels were prepared and analyzed. The average recoveries for 10 measurements of Cd for each acid type and each acid concentration, calculated as described above, are summarized in Table 2. The uncertainties were estimated at a confidence level of 95%, by taking into consideration the variation both in sample preparation and in the measurement process.

The Cd recoveries obtained by Zeeman GFAAS were really quite acceptable, ranging from 81 to 105%. A general decrease in Cd recovery was observed as the concentration of inorganic acid increased, probably because of an increase in sample viscosity that yielded a lower, and more erratic, sam-

Table 2. Recovery (%)^a of Cd in different media

Medium	Acid:water ratio				Concentrated
	1:9	1:4	1:2	1:1	
HNO ₃	93.9 ± 2.4	91.7 ± 2.6	93.5 ± 3.1	91.1 ± 3.4	88.8 ± 4.0
HCl	96.8 ± 1.0	99.1 ± 1.4	96.5 ± 2.0	97.6 ± 3.1	83.7 ± 6.0
HF	99.6 ± 1.6	100.1 ± 2.2	98.0 ± 1.4	93.0 ± 2.5	89.2 ± 3.4
H ₂ SO ₄	89.1 ± 2.4	88.6 ± 2.9	83.9 ± 4.1	85.8 ± 6.6	81.7 ± 4.3
HClO ₄	100.6 ± 3.0	96.8 ± 4.1	—	—	—
Aqua regia	95.1 ± 2.6	95.4 ± 2.8	94.5 ± 2.8	86.7 ± 4.7	83.2 ± 4.6
CH ₃ COOH	100.9 ± 1.2	104.7 ± 3.8	95.1 ± 2.9	102.6 ± 3.8	103.8 ± 3.9

^a Each value is the average ± standard deviation; *n* = 10.

ple volume intake. This effect was also the reason for the increase in uncertainty with an increase in acid concentration. In extreme cases, 50% by volume (1:1), sensitivity and precision both degraded and, consequently, the resulting recoveries were significantly lower (at the 95% confidence level and 9 degrees of freedom), and the corresponding uncertainties were notably higher.

Acid type had a considerable influence on Cd recovery, causing a depressing effect that increased in the following order: HF or CH₃COOH HCl or HClO₄ aqua regia HNO₃ H₂SO₄ for moderate concentrations of acid, and CH₃COOH HF or HCl HNO₃ aqua regia H₂SO₄ for higher concentrations. Density was one of the factors that seemed to have a remarkable influence on these results.

Cd in acetic acid showed good recoveries in all cases, but the precision decreased with the concentration of acid. In this medium, samples must be analyzed within a few minutes because of liquid evaporation.

Recoveries of Cd in moderate concentrations of H₂SO₄, HNO₃, and aqua regia media were significantly low. In the case of H₂SO₄, they were caused by the high density and viscosity, even at an acid:water ratio of 1:9. In HNO₃ matrixes, the effect was remarkable for reasons that are unknown. In this context, another group of samples was prepared and analyzed in an HNO₃ solution with an acid:water ratio of 1:19; an average Cd recovery of 98.4 ± 2.7% was obtained. This value is not significantly different from that obtained for Cd in

0.5M HNO₃ (with an acid:water ratio of approximately 1:28). From the data obtained for different concentrations of HNO₃, it can be concluded that this acid produces a depressing effect at a concentration lower than those needed for other acid types. Finally, the slightly low recoveries obtained for Cd in aqua regia can be explained by the contribution of HNO₃.

Because sequential extraction procedures are being widely used to understand the behavior of Cd in the environment, the effects of other media on Cd recoveries were evaluated. The protocol proposed by the Measurements and Testing Program of the European Commission as a sequential leaching scheme includes the following media: 0.11M acetic acid in the first step, 0.1M hydroxylammonium chloride in the second extraction, and 1M ammonium acetate in the third extraction. The final residual solid was digested according to the procedure described above for total Cd determination. The influence of these media was estimated by preparing and analyzing 10 solutions containing Cd at 5 g/L in each of these media. The Cd recoveries obtained are shown in Table 3. There are only statistical differences, at a confidence level of 95%, between the data obtained with 1M ammonium acetate and those obtained with standard solution (0.5M HNO₃ medium). This finding could be due to the relatively high salt concentration with respect to the other media. This result is consistent with the small differences already observed between the standard additions method and calibration with synthetic standards (10). It can be concluded from this study that the behavior of Cd in these media is similar to that observed in 0.5M HNO₃; therefore, there is no marked influence of these media.

Table 3. Recovery of Cd in different media

Medium	Recovery, % ^a
Acetic acid, 0.11M	100.2 ± 1.9
Hydroxylammonium chloride, 0.1M	102.8 ± 4.5
Ammonium acetate, 1M	92.0 ± 4.3
Digestion medium	97.9 ± 3.4

^a Each value is the average ± standard deviation; *n* = 10.

Application to the Environmental Field

The previously proposed method (9) was optimized for certain matrixes: soil, sediment, and coal fly ash. Because a broad variety of matrix types are included in the environmental field, applications to a great number of varied environmental matrixes were tested. Therefore, 14 reference materials including different matrixes with a wide range of Cd concentrations (3 orders of magnitude) were chosen (Table 4).

Table 4. Certified values and values found by the proposed method for a series of reference materials

Supplier	Reference material		Value, g Cd/g sample	
	ID	Type	Certified ^a	Found ^b
Sediments				
BCR	CRM 280	Lake	1.6 ± 0.1	1.72 ± 0.13
BCR	CRM 320	River	0.533 ± 0.026	0.547 ± 0.026
Soils				
NIST	SRM 2709	San Joaquin soil	0.38 ± 0.01	0.377 ± 0.010
NIST	SRM 2711	Montana soil	41.7 ± 0.25	40.2 ± 1.7
Sewage sludges				
BCR	CRM 146	Sewage sludge of industrial origin	77.7 ± 2.6	77.8 ± 5.2
BCR	CRM 144	Sewage sludge of domestic origin	3.41 ± 0.25	3.32 ± 0.21
Coals and ashes				
BCR	CRM 176	City waste incineration ash	470 ± 9	471 ± 27
NIST	SRM 1633a	Coal fly ash	1.00 ± 0.15	1.01 ± 0.03
BCR	CRM 040	Coal	0.11 ± 0.02	0.119 ± 0.015
Plant tissues				
NIST	SRM 1575	Pine needles	<0.5	0.235 ± 0.029
BCR	CRM 062	Olea europea (olive leaves)	0.10 ± 0.02	0.103 ± 0.009
BCR	CRM 279	Ulva lactuca (sea lettuce)	0.274 ± 0.022	0.286 ± 0.029
Animal tissues				
BCR	CRM 278	Mussel tissue	0.34 ± 0.02	0.339 ± 0.028
NRCC	DOLT-2	Dogfish liver	20.8 ± 0.5	20.7 ± 0.6

^a The uncertainties represent 95% tolerance limits.

^b The uncertainties represent 95% tolerance limits for an individual subsample of 250 mg.

They were supplied by the Community Bureau of Reference of the Commission of the European Communities (BCR), the National Institute of Standards and Technology (NIST) of the United States, and the National Research Council of Canada (NRCC). Lake and river sediments, 2 soils differing in Cd concentration by 2 orders of magnitude, sewage sludges of industrial and domestic origin, a coal, coal fly, and city waste incineration ashes, aquatic and nonaquatic vegetables, as well as 2 animal tissues were analyzed.

The dissolution procedure was the same for all the materials studied. After microwave digestion treatment, a considerable residue could remain, depending on the sample composition. This happened, for example, for samples of coal and coal fly ash. In any case, the sample solution was always filtered. With the same treatment for all samples, matrix differences were reduced, so that sample behavior in the measurement step became similar.

Table 4 shows the average concentrations of Cd obtained for the different reference materials studied, together with the corresponding uncertainties expressed for a 95% tolerance limit. Both were calculated from 6 results obtained for samples subjected to the complete analytical procedure (from the dissolution step to the measurement step). As shown in Table 4, the results are in very good agreement with the certified

values. There are no significant differences at a 95% confidence level, with an average error of about 3%. The uncertainties obtained for some materials with elevated Cd content are markedly higher than those for the certified values. These differences can be attributed to the use of other analytical techniques more suitable at these concentration levels, so as to avoid the introduction of dilution errors.

Evaluation of the Method

In the present work, a method proposed for the determination of trace levels of Cd was tested with a series of different and representative environmental samples. The results obtained show that the same dissolution and determination procedure is useful for such different matrixes. In particular, the matrix modifier worked very well for all the materials.

Considerable changes in absorbance peak and background shape were observed, when the same graphite tube atomizer was used in a large number of assays, and when different types of samples or interfering elements were tested. These problems were totally overcome by using both peak areas (integrated absorbances) and the Zeeman effect background correction. A critical parameter of this method is the establishment of a careful and suitable position of both the

graphite tube and the pyrolytic forked platform, as well as an adequate introduction of the sample by the injector.

On the other hand, results proved that it was not necessary to apply the standard additions method, because the different matrixes did not significantly influence the slope of the calibration curve. Consequently, the detection limit is independent of the type of sample and was estimated to be 26 ng/g (corresponding to 0.13 g/L). If a decrease in the detection limit is required, amounts 250 mg sample could be weighed. It was advisable to extend the range of the calibration curve to 0.5–10 g/L in the application of the direct method to the different environmental matrixes. In this case, the calibration curve is not a straight line. This problem was easily overcome with a quadratic function. By increasing the sample volume taken by the injector to 10 L, the capability of the instrument to dilute the samples is increased to cover a larger range of concentrations. The final parameters used are summarized in the *Experimental* section entitled *Determination of Cd*.

Conclusions

A general and versatile method for sample dissolution and GFAAS determination of Cd over a wide range of concentrations (0.1–500 g/g) was developed and tested in analyses of a series of representative environmental materials. The proposed method provided good results with the use of the same calibration curve and only 1 modifier to minimize the influence of the different matrixes. Peak area measurements (integrated absorbances) and Zeeman effect background correction gave consistent concentration results.

The influence of 49 possible interfering elements was found to be practically nonexistent, because the Cd recoveries obtained in all cases ranged from 93 to 106% for an interference/analyte concentration ratio of up to 10^5 . The versatility of the proposed method was also tested for different media such as HNO₃, HCl, HF, H₂SO₄, HClO₄, aqua regia, and acetic acid. Their influence was not very remarkable, with errors of 20%, even for concentrated acid media. A general decrease in Cd recovery and precision was observed as the acid concentration increased. With respect to the type of acid, H₂SO₄, HNO₃, and aqua regia showed a greater depressing effect on

the Cd absorbances than did the other acids at moderate concentrations. Widely used sequential extraction media were also tested. Although 0.11M acetic acid, 0.1M hydroxylammonium chloride, and the medium resulting from the digestion of the final residue scarcely affected the determination of Cd, 1M ammonium acetate caused a weak reduction of the measured absorbances.

Because concomitant elements and different media had no marked influence on the determination of Cd, the versatility of the proposed method was checked by analysis of a group of various reference materials with a wide range of concentrations. The results obtained were in good agreement with the certified values.

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