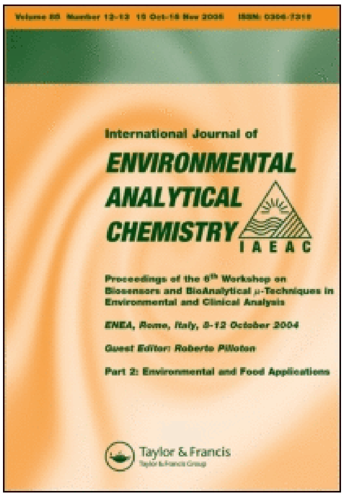

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Cadmium Determination in Soil Extracts by Furnace Atomic Absorption†

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A method for the direct determination of Cd in soil extracts by graphite furnace atomic absorption spectrosopy (GFAAS) has been developed. Optimum operating conditions, analyte modifiers and matrix interferences have been investigated. Characteristic amounts are 0.34 pg for siliceous samples and 0.45 pg for calcareous soils. The precision has been based on ten replicate readings in standards, and was 1.6%. Cd has been determined by the proposed methods and the results have been compared with those obtained by ICP technique.

KEY WORDS: Cd, graphite furnace atomic absorption spectroscopy, soil extracts.

INTRODUCTION

It is of great interest to study the environmental behaviour of Cd since it is one of the most toxic elements to living organisms, and its concentration increases with industrial development. The amount of Cd in soil usually is very low (< 1 ppm). Nevertheless, it can increase

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as a consequence of air pollution, by the use of some inorganic fertilizers and by the use of sewage sludges.

Cd is not considered as an essential element. It is one of the most widely studied metals in connection with sewage sludge used as a fertilizer. Its importance in the food chain is due especially to the ease of uptake in plants and its accumulation.

Numerous studies have been conducted to determine Cd implications when sewage sludge is used as a fertilizer.[1,2,3]

Levels of toxic metals in extracts are usually below the sensitivity of the techniques traditionally used in agricultural analysis (colorimetry,[4] optical emission spectrography,[5,6,7] flame atomic absorption spectrometry[5]), therefore pre-concentration steps must be used.

At present, two techniques with detection limits at μg/L level, such as graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES), have been introduced in this analysis area.

Direct determination of trace elements in soil extracts by GFAAS is troublesome because the high salt content leads to spectral and chemical interferences,[8,9,10] injection problems and presence of multiple peaks.[11] Another unrecognized source of interference was char loss resulting from the salt matrix.

The determination of Cd is especially difficult because of his volatility; the use of selective volatization sometimes makes possible to obtain a Cd peak before the background, especially when using pyrolytic tubes.[12]

There is a large bibliography for Cd in soil extracts, but normally it contains a chelation-extraction step prior to determination to reduce matrix interferences;[8,11,13–17] few methods use a direct determination.[18]

The aim of this work is to develop a direct method of Cd analysis by GFAAS, in order to determine the relationship between sewage sludge fertilization, Cd availability in soils and Cd absorption by crops.

EXPERIMENTAL SECTION

Apparatus and working conditions

A VARIAN, model 875, atomic absorption spectrophotometer

TABLE I
Working conditions

λ (nm)				228.8
Spectral band width (nm)				0.5 R
Lamp current (ma)				3.5
D_2 arc mode				
Internal Ar flow (l/min)				3
Automatic injection (μl)				20
Pyrolytically coated graphite tubes (partitioned)				
Peak height mode				
Drying	75°C	5 S		
	95°C	40 S		
	120°C	15 S		
Calcination	300°C	2 S		
	300°C	20 S		
	300°C	2 S	Gas stop	
Atomization	1200°C	0.5 S	Gas stop	Read
	1200°C	2 S	Gas stop	Read
	1200°C	2 S		
Cleaning step	2800°C	2 S		

equipped with a GTA-95 graphite furnace with graphic video mode display and sampling dispenser has been used in the study. Background correction has been made using a deuterium arc. Pyrolytically coated partitioned graphite tubes (VARIAN, ref. 63-100008-00) have been used. Recommended working conditions are given in Table I.

Reagents

All the labware used has been soaked in dilute HNO_3 at minimum 48 h and has been rinsed with distilled-deionised water ten times. Autosampler cups have also been conditioned with diluted nitric acid. Samples and standards have been stored in polyethilene bottles.

"Suprapur" grade acids (Merck) have been used. Inorganic compound solution used for standard and sample preparation have been reagent grade obtained from Baker and Merck. The Cd solution 1.0 g/l was prepared by dissolving cadmium oxide according to EPA methods.[19] Solutions prepared for characterization of interelement effects have been prepared from “Specpure” chemicals (Johnson Matthey Co.).

Sampling

The soils employed have been taken from the A_p horizons of two XERUFLUVENT with substantial different characteristics as pH, CEC and texture. The chemical composition and physicochemical properties are reflected in Table II.

TABLE II

Chemical composition and physico-chemical properties

	Soil A	Soil B
Organic matter (%)	0.77	1.74
N—total (%)	0.04	0.12
P_2O_5 available (μg/g)	257	287
K_2O available (μg/g)	122	243
CO available (μg/g)	760	3890
MgO available (μg/g)	55	140
PH_{H_2O}	5.64	7.81
Elect. conduct. (1/5) (umhos/cm)	20	80
C.E.C. (meq./100 g)	2.84	12.50
CO_3^{2-}(%)	—	7.75
Textural class	Sandy loam	Sandy clay loam

Soil extraction procedure

Cd extraction has been performed by the method of Lakanen and Ervio[20] using EDTA. 10 g of air-dry soil have been shaken with 100 ml of 0.02 M EDTA—1 M ammonium acetate (pH = 4.8), during 30 minutes.

A determination of major compounds extracted in the soils have given these contents:

Sample A Ca 61 μg/ml, Si 50 μg/ml, Al 21 μg/ml, Fe 16 μg/ml, Mg 7 μg/ml, K 1 μg/ml and Na < 1 μg/ml.

Sample B Ca 2132 μg/ml, K 28 μg/ml, Mg 18 μg/ml, Al 15 μg/ml, Si 15 μg/ml, Fe 6 μg/ml and Na 1 μg/ml.

Procedure

Cd determination is carried out after a 25-fold sample dilution using a calibration method with standards ranging 0.2–4 μg/l Cd in 1:25 extractant solution. 1% HNO_3, 100 μg/ml Mo and 1.5% H_2O_2 must be added to standards and samples as matrix modifier.

In calcareous samples the addition of 1500 μg/ml Ca to standards and samples is recommended.

RESULTS AND DISCUSSION

Optimum thermal conditions and modification technique

The experimental method proposed by Weltz[21] and Chakrabarti[22] has been used. Decomposition-atomization curves for Cd in soil extract are shown in Figure 1. The loss of Cd in the calcination step

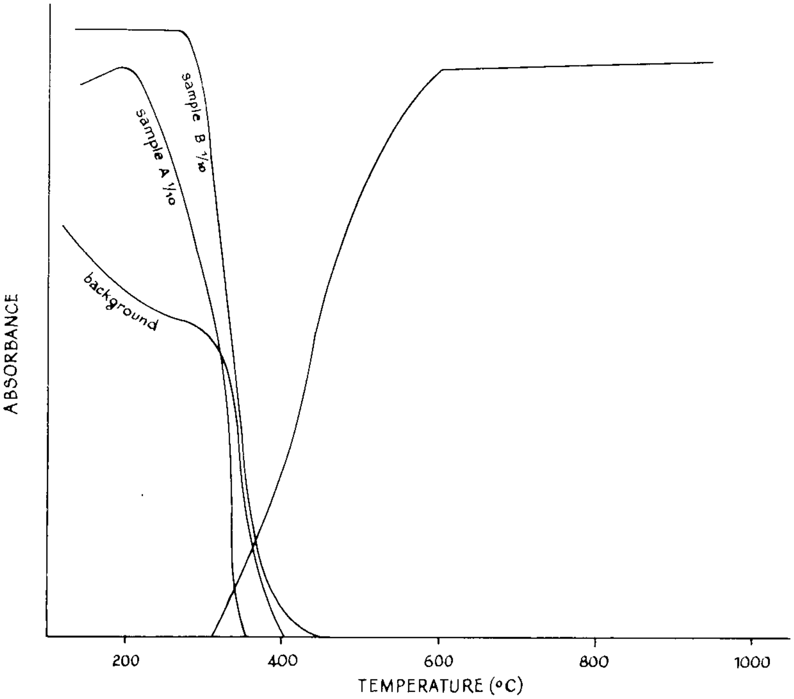

FIGURE 1 Decomposition-atomization curves for Cd in EDTA extract. Dilution 1/10. A-siliceous soil, B-calcareous soil.

has been severe, especially in siliceous soil extracts, making difficult any charing process.

The use of an analyte modifier has been tried. Among the modifiers used for Cd, phosphates are the most recommended,[23] but their use leads to a structured background that the continuum-D_2 cannot correct well. This interference was reported by Saeed and Thomassen,[24] and Fernandez and Giddings;[25] Calcium phosphate has been found to be the source for this spectral interference.

Henn[26] has reported the addition of Mo in presence of H_2O_2 to minimize matrix effects in the determination of Se, Pb and Cd. The effect of the metal is probably the formation of the non-volatile metal-anion in the furnace.

The authors have often verified, in the laboratory, the efficiency of Mo as modifier for Cd and Pb.

Figure 2 shows the effect of the addition of 1% HNO_3, 100 μg/ml Mo and 1.5% H_2O_2 on the volatility of Cd when it is applied to soil extract. The loss of Cd, when Mo is present, begins at 400°C, and the background is greatly reduced; That permits a correct decomposition treatment of samples.

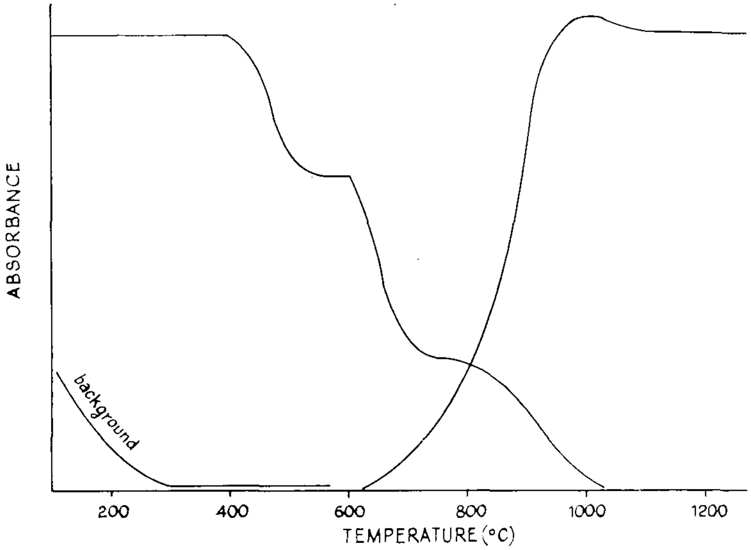

FIGURE 2 Decomposition-atomization curves for Cd in EDTA extract (siliceous soil, dil. 1/10) with analyte modification by adding 1% HNO_3, 100 μg/ml Mo and 1.5% H_2O_2.

The optimum atomization temperature has been investigated using atomization curves of absorbance and background signal. Absorbance remains constant when a temperature of 1000°C (Figure 2) is exceeded, and 1200°C has been chosen for a good reproducibility. At this temperature, the background absorbance is zero.

The low atomization temperature used necessitates a clean-up step at 2800°C.

The minimum atomization temperature that gives maximum absorbance (1000°C) has been very low when compared to the temperatures used in the literature (ranging from 1600° to 2000°) and has been related to a short atomizer length or very fast heating ramps (2000°C s^{-1}).[27]

Matrix interference study

The interference study has been made with Ca, Mg, Na, K, Fe, Al and Si (as nitrates), using a solution of 1 μg/l Cd. The results obtained are given in Figure 3.

The interference effects are important and must be considered, but, as we have been working with a 25-fold dilution, only Ca in calcareous soil samples must be taken into account.

Precision and sensitivity

The relative standard deviation (RSD) of ten absorbance readings on the same solution at 1 μg/l Cd level are: 1.53% in 1% HNO_3, 1.65% in 1% $HNO_3 + Mo + H_2O_2 +$ extractant, 1.98% and 2.43% in siliceous and calcareous samples after a 25-fold dilution.

The calibration curves obtained with standards in 1% HNO_3 and diluted matrix have a medium slope value of 0.201 and 0.221 $(\mu g/1)^{-1}$, respectively. Medium slope values for soil samples, diluted 1/25, analyzed by standard additions are 0.223 and 1.162 $(\mu g/l)^{-1}$.

Characteristic amounts are 0.398 pg and 0.345 pg for 1% HNO_3 and diluted matrix solutions, 0.335 pg and 0.447 pg for siliceous and calcareous soil extracts, respectively. The recommended analytical range for analysis is 0.2 μg/1–4 μg/l Cd. The lower limit is set at ten times the characteristic amount with a sample injection of 20 μl.

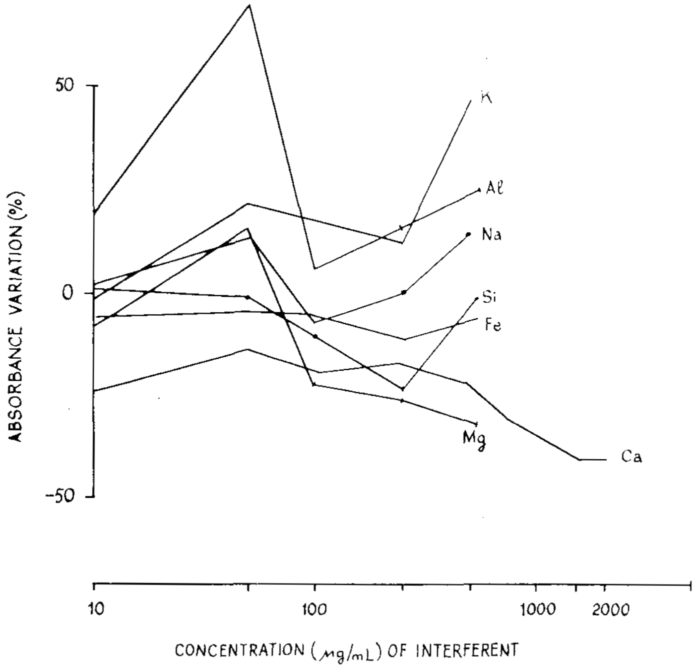

FIGURE 3 Absorbance variation of Cd (1 μg/l) as a function of interferent metal concentration.

Accuracy

In order to know the accuracy, samples have been analyzed by ICP and GFAAS using addition and calibration methods.

The calibration has been carried out by two methods: (a) with standards prepared with Cd and diluted extractant solution, and (b) with standards prepared with Cd, diluted extractant solution and 1500 μg/ml Ca. In the last method, 1500 μg/ml Ca has been also added to the samples. The results obtained are given in Table III.

This table shows that results obtained for Cd by ICP and GFAAS agree closely.

ANALYSIS OF FERTILIZED SOILS

Analysis of available Cd in soils, and Cd uptake by barley crops after fertilization with 5.10 and 20 Tm/Ha of sewage sludge,[28] have

TABLE III

Summary of GFAAS and ICP analysis of Cd on EDTA extracts of soils (Concentrations: μg/g in air dry material)

	ICP	Addition	GFAAS Calibration[a]	Calibration[b]
Siliceous soil (Sample A)	0.095	0.101	0.094	0.091
Calcareous soil (Sample B)	0.149	0.164	0.125	0.158

[a] Standards prepared with Cd + extractant.

[b] Standards prepared with Cd + 1500 μg/ml Ca.

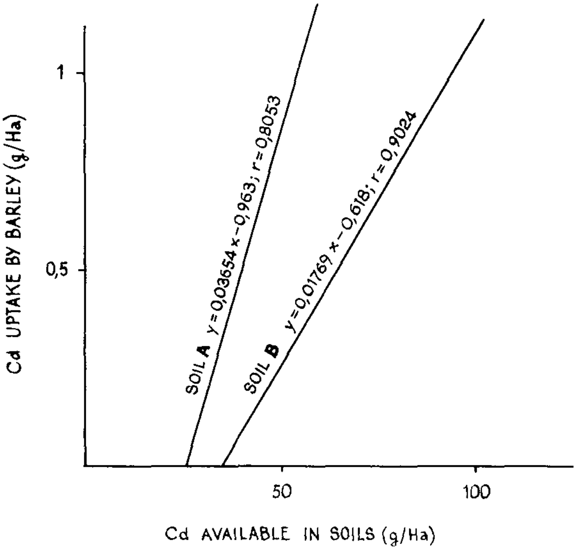

FIGURE 4 Correlation between Cd extractable and Cd uptake.

been carried out using proposed methods. Highly significant correlations between Cd extractable and Cd uptake are shown in Figure 4.

CONCLUSIONS

The most important object of this work has been to show that Cd can be determined directly by GFAAS in a very complex matrix, with correct precision and accuracy, avoiding previous extraction procedures which require extensive sample handling with the risk of contamination problems.

The use of an ultrafast ramp heating ($\geqq 2000\,\mathrm{C}^\circ s^{-1}$), the addition of $\mathrm{Mo+H_2O_2+HNO_3}$ as matrix modifier and an accurate optimization of instrumental parameters, are the most important features to succeed in this determination.

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