Cadmium Levels in Food and Feed Crops, Determined by Electrothermal Atomic Absorption Spectrometry

Carmen Cabrera,*,† María L. Lorenzo,† Carmen Gallego,† María C. López,† and Enrique Lillo‡

Department of Nutrition and Bromatology, School of Pharmacy, University of Granada, E-18071 Granada, Spain, and Laboratorio Agrario de Granada, Junta de Andalucia, E-18014 Atarfe, Spain

An efficient method for the determination of nanogram levels of cadmium in food and feed crops is described. Plant samples from the coast of the province of Granada (Spain) were analyzed by electrothermal atomic absorption spectrometry of tissues previously treated in a microwave acid bomb. The samples were injected through a graphite tube with a L'vov platform. The concentrations of cadmium in food and feed crops ranged from ND (not detectable) to 8.7 ng/g.

INTRODUCTION

Cadmium, a rare element in the earth's crust, is extensively used for industrial purposes. Contamination of the soil, atmosphere, water, and plants and of foodstuffs with this toxic metal has therefore become widespread (Robards and Worsfold, 1991; Concon, 1988).

Cadmium ions are readily transferred from the soil to plants, which absorb the element and accumulate it to different degrees, depending on the species. This process is favored by low soil pH values, probably as a result of the increase in the exchangeable portion of Cd (Derache, 1990). Recent studies have documented contamination of cereals and vegetables (lettuce and radish) growing in soils to which cadmium dioxide had been added, and further investigations have attempted to quantify the transfer of this compound to tomato, string bean, and radish (Derache, 1990; Environmental Protection Agency, 1975). Cadmium accumulation by plants is a continuous process that requires no particular threshold value of Cd in the soil and has been shown to take place at concentrations as low as 0.03 ng/g.

The risk of Cd entering the earth's biological chain has increased in recent years, because of industrial wastes and the widespread use of phosphates and sewage sludge as fertilizers. All of these sources contribute to the slight but systematic contamination of all vegetable foods, in which Cd levels have been found to range from 5 ng/g to as high as 100 ng/g (Martin and Coughtrey, 1982; FAO/WHO, 1989).

Although this contamination may go unnoticed in studies that concentrate on specific food types, it becomes evident when the consumption of large amounts of certain foods causes the dietary intake of Cd to reach the maximum allowable levels.

Considered as an analytical sample, any type of plant represents a complex matrix requiring previous mineralization before most of the analytical techniques proposed thus far can be used. The most widely accepted approach currently seems to be the use of microwaves to accelerate digestion of the sample, which is placed in a closed recipient and subjected to acid and high pressure (Uhrberg, 1982; Van Eenbergen and Brunix, 1978; Okamoto and Fuwa, 1984; Kingston and Jassie, 1986; Stripp and Bogen, 1989).

* Author to whom correspondence should be addressed (fax +34-58-243869).

† University of Granada.

‡ Junta de Andalucia.

Table I. Furnace Conditions for the Determination of Cadmium in Food and Feed Crops by Electrothermal Atomic Absorption Spectrometry

step	temp, °C	ramp time, s	hold time, s	gas flow rate, mL of Ar min^{-1}
dry	130	40	10	50
char	450	30	30	50
atomize	1600	1	4	stop
clean	2650	1	2	50

The analytical techniques used most frequently to measure Cd in foodstuffs are atomic emission, fluorescence, or absorption spectroscopy (AAS) (Robards and Worsfold, 1991), while electrothermal atomization (ETA) has become the most widely used method of measuring trace elements in foodstuffs (AOAC, 1989; Dabeka and Makenzie, 1986; Vidal, 1990; Lynch and Littlejohn, 1990; Welz and Schlemmer, 1987).

In this paper an optimal method for the determination of Cd in food and feed crops with AAS-ETA is described. The method is based on an optimized time–temperature program for drying, charring, and atomization and on corrections to adjust for interferences and other factors that might affect accuracy and precision.

EXPERIMENTAL PROCEDURES

Apparatus. A double-beam atomic absorption spectrophotometer (Perkin-Elmer 2380) was used with a deuterium arc background corrector and an 11-mA hollow cathode lamp, at a slit width of 0.7 nm. Atomization was performed under the conditions shown in Table I, using a Perkin-Elmer HGA-400 furnace with a pyrolytic graphite furnace tube and a L'vov platform at 228.8 nm. The samples were injected manually with a Pipetman micropipet. Signals were recorded in peak-height mode with a Perkin-Elmer 024 potentiometric recorder. The samples were mineralized in a Parr 4782 microwave acid digestion bomb and a Moulinex FM-460 microwave oven.

Reagents. All solutions were prepared with ultrapure water with a specific resistivity of 18 MΩ/cm, obtained by filtering double-distilled water through a Milli-Q purifier (Millipore) immediately before use. The standard solution of Cd was used at a concentration of 1 mg/mL. Nitric acid (65%) (Merck, Suprapure), vanadium pentaoxide, and ammonium molybdate (Merck, analytical grade) were also used. The reference standard consisted of citrus leaves [National Bureau of Standards (NBS), standard reference material SRM 1572] with a certified Cd content of 0.03 ± 0.01 μg/g.

Samples. All samples were obtained in the field from farms located along the coast of the province of Granada (southern Spain), in an area where the predominant crops are sugar cane (*Saccharum officinarum*), corn (*Zea mays*), and garden vegetables.

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Table II. Statistical Analysis of the Results of Determinations of Cadmium in Food and Feed Crops by Electrothermal Atomic Absorption Spectrophotometry

sample	$\bar{x}$[a]	σ[b]	σ_m[c]	$\bar{x} \pm \sigma_m t$	$\sigma_m t/\bar{x}$, %
sweet corn	0.0355	9.7182×10^{-4}	3.0732×10^{-4}	$(0.0355 \pm 6.9515) \times 10^{-4}$	1.96
sugar cane	0.0207	1.1595×10^{-3}	3.6666×10^{-4}	$(0.0207 \pm 8.294) \times 10^{-4}$	4.00

[a] $\bar{x}$, mean value of 10 determinations. [b] σ, standard deviation for 10 replicate determinations. [c] σ_m, standard error of the mean. The value of Student's t was 2.262 for both samples.

Table III. Mean Concentrations of Cadmium in Food and Feed Crops Grown on the Coast of the Province of Granada (Spain)

sample	mean,[a] ng/g	range,[a] ng/g
sugar cane (*S. officinarum*)	0.540	ND–1.305
sweet corn (*Z. mays*)	3.400	ND–8.689
potato (*Solanum tuberosum*)	0.180	ND–0.588
green bean (*Phaseolus vulgaris*)	0.235	0.145–0.303
banana (*Musa paradisiaca*)	0.765	0.563–0.956
lettuce (*Lactuca sativa*)	5.910	5.276–6.551
tomato (*Lycopersicum esculentum*)	0.510	0.507–0.516

[a] Fresh weight.

The samples were thoroughly washed or peeled and then dried under controlled temperature conditions. All analyses were performed in triplicate, using the edible portions only of each sample.

Procedure. Amounts of 250 mg of dried, homogenized sample were treated with 2.5 mL of nitric acid and a few micrograms of vanadium pentaoxide as a catalyst and then digested in the microwave acid digestion bomb. Mineralization was complete in 90 s with the oven at its highest setting. After the digestion bomb was cooled by freezing at −18 °C for 45 min, the solution was diluted with 25 mL of ultrapure water. An aliquot of 20 μL was injected into the tube, which had been treated with saturated ammonium molybdate to avoid the formation of refractory carbides, and run under the optimized conditions shown in Table I. The conditions were optimized on the basis of time–temperature studies using a certified standard.

RESULTS AND DISCUSSION

Graphite Furnace Program Optimization. Mineralization of the matrix was complete after heating to 450 °C for 60 s. The atomization temperature that yielded maximum signals was 1600 °C for an integration time of 6 s. Stopping the flow at this point enhanced sensitivity without compromising the sensitivity or the lifetime of the tube. The use of a L'vov platform gave more reproducible results.

Calibration and Analytical Characteristics. The calibration plot was obtained from a standard solution of 1 mg/mL and successive dilutions with 10% nitric acid, ranging from 0.05 to 0.20 ng/mL and prepared from a working solution of 1 μg/mL. These solutions along with the blank (a few micrograms of vanadium pentaoxide, 2.5 mL of nitric acid, and ultrapure water to a total volume of 25 mL) were subjected to the same acid digestion bomb treatment as the samples.

The standard addition method was used to detect possible interference due to matrix effects. The range of Cd concentrations was assayed in five different food and feed crop species (corn, sugar cane, green bean, potato, and banana) chosen randomly from among all samples. Amounts ranging from 0.05 to 0.20 ng/g were added to 250-mg fractions of samples and to blanks, and then all samples and blanks were mineralized and diluted according to the same procedure. The slopes of the calibration lines for spiked samples were similar to the slope of the calibration line for the standard in acid medium; thus, matrix effects were considered to be negligible.

The equation for the calibration plot was absorbance = $2.5 \times 10^{-3} + 0.374$[Cd (ng/g)], with $r = 0.9982$ and $\alpha = 1\%$ (α, level of significance). The equation was linear from 0.008 ng/mL to 0.1 μg/mL.

The accuracy of the method was tested with recovery assays. Mean recovery was found to be 98.63% for four determinations in five different species. Recovery of the NBS certified standard was 0.027 ± 0.02 μg/g ($n = 10$).

The technique was accurate and reproducible. The results of 10 determinations in two different species were analyzed statistically as described in Stiel (1982). The results of the precision test are summarized in Table II.

Application of the Method to Food and Feed Crop Samples from the Coast of Granada. The values obtained in fresh samples ranged from ND (not detectable) to 8.7 ng/g (Table III).

The ultramicrotechnique described above provided highly sensitive measurements with a low limit of detection, making it suitable for rapid, straightforward analyses at the range of concentrations found in the food samples tested. Under the optimized conditions, most sources of interference from the matrix and from nonspecific absorptions were corrected for, as shown by the results of the standard addition analysis.

Mineralization in the microwave acid digestion bomb was complete after 90 s, a significant advantage over other procedures that require hours or days. The small volume of acid used and the minimal handling of few reagents decrease the chances of contamination, an important factor in work with trace elements.

This method is appropriate for routine laboratory analyses. Moreover, it provided information on the environmental impact of Cd as measured by the concentration of the element in widely grown food and feed crops.

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LITERATURE CITED

AOAC. *Official Methods of Analysis of the Association of Official Analytical Chemists*, 15th ed.; Helrich, L., Ed.; Association of Official Analytical Chemists: Arlington, VA, 1990; 262 pp.

Concon, J. M. In *Food Toxicology, Part B: Contaminants and Additives*; Dekker: New York, 1988; 1043 pp.

Dabeka, R. W.; Makenzie, A. D. Graphite-furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium in Food after Nitric-perchloric Acid Digestion and Coprecipitation with APDC. *J. Spectrosc.* **1986**, *31*, 44–52.

Derache, J. *Toxicología y Seguridad de los Alimentos*; Omega: Barcelona, 1990; pp 133–163.

Environmental Protection Agency. *Technical and microeconomic analysis of cadmium and its compounds*; U.S. Environmental Protection Agency, Office of Toxic Substances: Washington, DC, 1975; 560/3-75-005.

FAO/WHO. *33rd Meeting of the Joint FAO/WHO Expert Committee on Food Additives*; Food and Agriculture Organization of the World Health Organization: Geneva, 1989.

Kingston, H. M.; Jassie, L. B. Microwave Energy for Acid Decomposition at Elevated Temperatures and Pressures Using Biological and Botanical Samples. *Anal. Chem.* **1986**, *58*, 2534–41.

Lynch, S.; Littlejohn, D. Development of a Slurry Atomization Method for the Determination of Cadmium in Food Samples by Electrothermal Atomization Atomic-absorption Spectrometry. *Talanta* **1990**, *37*, 825–30.

Martin, M. H.; Coughtrey, P. J. *Biological monitoring of heavy metal pollution*; Applied Science: New York, 1982.

Okamoto, K.; Fuwa, K. Low-Contamination Digestion Bomb Method Using a Teflon Double Vessel for Biological Materials. *Anal. Chem.* **1984**, *56*, 1758–60.

Robards, K.; Worsfold, P. Cadmium: Toxicology and Analysis. A Review. *Analyst* **1991**, *116*, 549–68.

Stiel, R. G. *Principles and Procedures of Statistics*; McGraw-Hill: London, 1982.

Stripp, R. A.; Bogen, D. C. The Rapid Decomposition of Biological Materials by Using a Microwave Acid Digestion Bomb. *J. Anal. Toxicol.* **1989**, *13*, 57–59.

Uhrberg, R. Acid digestion Bomb for Biological Samples. *Anal. Chem.* **1982**, *54*, 1906–08.

Van Eenbergen, A.; Brunix, E. Losses of Elements during Sample Decomposition in an Acid Digestion Bomb. *Anal. Chim. Acta* **1978**, *98*, 405–06.

Vidal, J. C. Determination of Cadmium by Electrothermal Atomisation Atomic Absorption Spectrometry after Electrodeposition on a L'vov Platform. *Analyst* **1990**, *115*, 539–43.

Welz, B.; Schlemmer, G. Determination of As, Se, and Cd in Marine Biological Tissue Samples Using a Stabilized Temperature Platform Furnace and Comparing Deuterium Arc with Zeeman-effect Background Correction Atomic Absorption Spectrometry. *J. Anal. At. Spectrom.* **1987**, *1*, 119–21.

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