

Determination of Mercury in Crops by Cold Vapor Atomic Absorption Spectrometry after Microwave Dissolution

Miguel Navarro-Alarcón,* Maria C. López-Martínez, Mercedes Sánchez-Viñas,† and Herminia López-García de la Serrana

Department of Nutrition and Bromatology, Faculty of Pharmacy, University of Granada, E-18012 Granada, Spain

The toxicological significance of low mercury concentrations in agricultural crops requires a sensitive, accurate, and precise method for mercury analysis at the parts per billion level. A procedure utilizing microwave dissolution in a closed Teflon bomb followed by cold vapor atomic absorption spectrometry has been developed for the routine analysis of mercury in different samples of sugar cane, sweet corn, potato, green bean, banana, lettuce, and tomato. The limit of detection is 0.195 ng/mL. Sample recoveries, precision studies, and analyses of NBS reference material demonstrate the reliability and accuracy of this technique. A summary of results for 51 crop samples, which ranged from 0.005 to 0.215 $\mu\text{g/g}$, is reported.

INTRODUCTION

The greatest sources of mercury pollution are human activity and modern technology. There is international concern about human intake of toxic trace elements such as mercury. Intake of relatively low doses of this element over a long period can lead to malfunction of organs and chronic toxicity (Concon, 1988). This has led, in recent years, to growing interest in the analysis of Hg levels in foodstuffs (Cobs et al., 1985; Gunderson, 1988; Surma-Aho and Paasivirta, 1986; Teeny et al., 1984; Van Dokkum et al., 1989; Zook et al., 1976).

Mercury is in part ingested with the edible parts of agricultural and horticultural crops or derived products. Therefore, the determination of Hg in crops is necessary to evaluate its toxicological significance.

As an analytical sample, a plant is a complex matrix, and most methods of analysis proposed require previous mineralization (AOAC, 1990). Several modified wet digestion procedures have been recommended for vegetable samples, and many of these have been developed to reduce the time required for dissolution. Recently, there has been a great deal of interest in using microwave ovens to speed the digestion of a variety of sample matrices (Betinelli et al., 1989; Friel and Skinner, 1990; Stripp and Bogen, 1989; Van Delft and Vos, 1988; Vermeir et al., 1989). The merits of pressurized acid digestion in closed or semi-closed vessels, particularly the lower risks of contamination and volatilization losses, are widely recognized (AOAC, 1990; Okamoto and Fuwa, 1984; Uhrberg, 1982; Van Eenbergen and Brunix, 1978; Vermeir et al., 1988), and it is not surprising that such techniques are attracting considerable attention.

The most common procedures for the determination of Hg in crops are atomic emission, fluorescence, and absorption spectrometries. Cold vapor atomic absorption spectrometry (CV-AAS) has become the most widely used approach in Hg analyses in vegetable samples (AOAC, 1990; Chou and Naleway, 1984; Landi et al., 1990; Wiersma et al., 1986).

In this paper, microwave heating in sealed Teflon containers is applied for the dissolution of vegetable samples prior to the determination of traces of Hg by CV-AAS. By analyses of standard reference material, the precision and accuracy of the method were determined.

EXPERIMENTAL PROCEDURES

Apparatus. Ordinary laboratory glassware was employed. To eliminate absorbance due to detergents and samples, all glassware was washed after each use with tap water, soaked in nitric acid (at least overnight), and rinsed several times with ultrapure water.

Mineralization was performed with a Parr Instrument Co. 4782 microwave acid digestion bomb heated in a commercially available Moulinex FM-460 microwave oven. The oven power (15–100% power in 25% increments) and the time range (0 s to 60 min) can be present digitally. The oven used has a rotating antenna, so that the power is homogeneously distributed throughout the oven volume. The oven was placed in a laboratory fume hood.

All atomic absorption measurements of Hg were made with a Perkin-Elmer 2380 atomic absorption spectrophotometer equipped with a Perkin-Elmer MHS-10 hydride generator. Signals (peak height mode) were recorded on a Omniscrite D-5000 Bausch Lomb recorder.

Reagents. All inorganic acids used were Suprapure (Merck). All solutions were prepared with ultrapure water with a specific resistivity of 18 $\text{M}\Omega\text{ cm}$ obtained by filtering distilled water through a Millipore Milli-Q RO15 water purification system immediately before use.

Stock solution containing 1000 $\mu\text{g/mL}$ Hg was used to prepare calibration standards by serial dilutions immediately before use. Potassium permanganate solution was prepared by dissolving 5 g of KMnO_4 in 100 mL of water. Sodium tetrahydroborate solution was prepared by dissolving first 2.5 g of NaOH and then 7.5 g of NaBH_4 in 250 mL of water. This solution was stirred for 10 min and filtered before use. All reagents were of analytical grade.

The National Bureau of Standards (NBS) standard reference material used was citrus leaves (SRM 1572).

Samples. Fifty-one samples of vegetable origin food were obtained directly from horticultural crops of the south of the province of Granada (Spain). The samples were lyophilized and then ground manually to a fine powder in a mortar. Three 200-mg subsamples of each were taken for analysis.

Procedure. The lyophilized samples (200 mg) were treated with 2.5 mL of HNO_3 in the microwave acid digestion bomb. Mineralization was complete in 90 s with the oven at its highest setting. The digests were cooled, and the resulting solutions

* Address correspondence to this author.

† Present address: Department of Analytical Chemistry, Faculty of Sciences, University of Granada, E-18072 Granada, Spain.

Table I. Comparison of CV-AAS Mercury Measurements with NBS-Certified Concentrations

sample	Hg values, $\mu\text{g/g}$	
	certified ^a	determined ^a
NBS SRM 1572 (citrus leaves)	0.080 \pm 0.020	0.081 \pm 0.010

^a Mean and content range with 95% certainty based on 10 replicate analyses of 200-mg samples.

Table II. Recovery of Mercury from Spiked Crop Samples

sample	Hg present, μg	Hg added, μg	Hg found, μg	recovery, %
sugar cane 18 (<i>Saccharum officinarum</i>)	0.0287	0.0000	0.0290	101.05
	0.0287	0.0155	0.0442	100.00
	0.0287	0.0310	0.0607	101.68
	0.0287	0.0620	0.0907	100.00
sweet corn 1 (<i>Zea mays</i>)	0.1150	0.0000	1.1140	99.13
	0.1150	0.0910	0.2040	99.03
	0.1150	0.1590	0.2710	98.91
	0.1150	0.2270	0.3400	99.42

were diluted to volume with ultrapure water. A 10-mL aliquot was transferred to a reaction vessel, 1 mL of the KMnO_4 solution was added, and the vessel was connected to the MHS-10 system. The NaBH_4 solution was added and the Hg formed was swept with nitrogen into the quartz cuvette. The Hg signal was measured at 253.7 nm.

The calibration graph was obtained with a stock solution of 1000 $\mu\text{g/mL}$, using successive dilutions with 1.5% w/v HCl. Blanks ranging from 1 to 20 ng/mL were prepared from a working solution of 1 $\mu\text{g/mL}$. These dilutions, like the blank (HNO_3) were subjected to the same treatment as the samples. The data presented were corrected for blank values, which were usually very low for this method.

RESULTS AND DISCUSSION

Mineralization with the microwave acid digestion bomb technique was complete within 90 s, which represents a significant savings in time in comparison to other methods which require hours or even days for mineralization. The use of a small volume of acid and the simplicity of the entire procedure reduce the risk of contamination, an important factor in the determination of trace elements.

Interferences from the matrix appeared to be negligible, as verified by the standard addition method, which was performed on representative crop samples. Amounts ranging from 0.0 to 10.0 ng/mL were added to 200-mg fractions of sample and to the different blanks. All samples and blanks were mineralized and diluted with the same procedures.

The sensitivity found (equivalent to 0.0044 unit of absorbance) was 0.590 ng/mL. For the instrumental conditions used in sample analyses, our calculated analytical detection limit, defined as the Hg concentration corresponding to 3 times the standard deviation of the blank (Long and Winefordner, 1983), was 0.195 ng/mL. Both values were comparable to those reported by other authors and were adequate for the range of concentrations of the samples analyzed in this study.

The accuracy of the analytical method was established by determination of Hg in NBS standard reference material (SRM) and by quantitative recovery studies of submicrogram amounts of Hg added to the sample in the Teflon caps before digestion. Results of the analyses of NBS SRM 1572 (citrus leaves) are given in Table I. In all cases, the values obtained in the microwave dissolution method fall within the range of the NBS-certified values.

The data for the recovery studies are presented in Table II. The application of this method resulted in satisfactory recoveries for two samples investigated (Table II).

Table III. Precision Study

sample	mean Hg content, ^a $\mu\text{g/g}$	RSD, %
sugar cane 18 (<i>S. officinarum</i>)	0.0287 \pm 0.0029	10.10
sweet corn 1 (<i>Z. mays</i>)	0.1151 \pm 0.0078	6.78

^a Mean and standard deviation based on seven replicate analyses of 200-mg samples.

Table IV. Mercury Content of Crops As Determined with CV-AAS

sample	no. of samples	mean ^a	range ^a
sugar cane (<i>S. officinarum</i>)	24	0.035	0.010–0.121
sweet corn (<i>Z. mays</i>)	11	0.097	0.058–0.215
potato (<i>Solanum tuberosum</i>)	6	0.025	0.012–0.037
green bean (<i>Phaseolus vulgaris</i>)	4	0.009	0.006–0.015
banana (<i>Musa paradisiaca</i>)	2	0.152	0.106–0.198
lettuce (<i>Lactuca scariola</i>)	2	0.008	0.005–0.011
tomato (<i>Lycopersicon esculentum</i>)	2	0.006	0.005–0.007

^a Micrograms per gram (fresh weight).

The technique was found to be both precise and reproducible. Seven determinations in two different crop samples were treated statistically as described by Stiel (1982), and the results of the precision tests are summarized in Table III.

Table IV lists the means and ranges of the Hg contents in the vegetable origin foods studied. Of the 51 samples analyzed, the banana had the highest Hg levels, followed by sweet corn. The lowest Hg contents were those of tomato and lettuce.

In conclusion, the decomposition method is less complicated and time-consuming than conventional dissolution techniques. This method can be applied to any routine laboratory analysis used for quality control of crops and plants.

ACKNOWLEDGMENT

We thank the Department of Analytical Chemistry of the University of Granada (Spain) for their help and for placing the atomic absorption spectrometry equipment at our disposal.

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Received for review May 29, 1991. Accepted September 11, 1991.

Registry No. Hg, 7439-97-6.