Pergamon

0039-9140(94)00181-2

Talanta, Vol. 41, No. 12, pp. 2073–2078, 1994
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0039-9140/94 $7.00 + 0.00

DETERMINATION OF MERCURY IN MICROWAVE-DIGESTED SOIL BY LASER-EXCITED ATOMIC FLUORESCENCE SPECTROMETRY WITH ELECTROTHERMAL ATOMIZATION

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(*Received* 7 *April* 1994. *Revised* 27 *May* 1994. *Accepted* 31 *May* 1994)

Summary—A sample digestion procedure was developed which employs microwave heating of soil and sediment in concentrated nitric acid in a high-pressure closed vessel. Complete dissolution of mercury into the sample solution occurs within 5 min at 59 W/vessel without loss of analyte through overpressurization. Laser-excited atomic fluorescence spectrometry with electrothermal atomization (LEAFS–ETA) was used as the detection method. The scheme uses a two-step excitation, with $\lambda_1 = 253.7$ nm and $\lambda_2 = 435.8$ nm. Direct line fluorescence was measured at 546.2 nm. The absolute instrumental limit of detection was 14 fg; 1.4 pg/ml with a 10 μl sample injection. The recoveries of mercury in two spiked samples were 94 and 98%. The SRM 8406 (Mercury in River Sediment) was digested and analyzed for mercury, and the results (58.4 ± 1.8 ng/g) agreed well with the reference value of 60 ng/g. The results obtained by LEAFS–ETA with microwave sample digestion are in good agreement with those found by cold vapor atomic absorption spectrometry with EPA Series Method 245.5 sample digestion, which is one of the most commonly used methods for the determination of mercury in soil.

The contamination of the environment by mercury is an important ecological concern. Of particular interest is the analysis of mercury in soil and sediment because these media are sinks for pollutants, and levels of mercury measured there may indicate the significance of overall contamination for the system or area from which the sample was taken. Methods of sample digestion and detection must constantly be improved to provide reliable determination of lower concentrations of mercury in the environment. The Maximum Contaminant Level (MCL) set by the Environmental Protection Agency (EPA) for mercury in soil is currently 200 ng/g (ppb). Based on past EPA protocol, with improvements in methodology and instrumentation, the MCL can be reduced.

Many techniques have been used for the determination of mercury in environmental samples including colorimetry,[1] HPLC,[2] Zeeman graphite furnace atomic absorption spectrometry (AAS),[3] X-ray fluorescence spectrometry (XRF)[4] and helium microwave induced plasma (He-MIP) atomic emission spectrometry (AES).[5] The most commonly used technique for the analysis of mercury in soils, however, is cold vapor atomic absorption spectrometry (CVAAS), with sample digestion by an EPA-approved wet oxidation method. Like all wet oxidation methods used for soil decomposition, EPA Series Method 245.5 is very time consuming and laborious. The method requires a digestion time of 2 hr in a hot-water bath, and it utilizes many reagents which increase the possibility of contamination to the sample and to the environment after sample disposal. The technique of CVAAS is sensitive for mercury with a method detection limit of 0.2 ppb. However, in the CVAAS method a large sample volume of 50 ml is used which leads to a relatively high absolute detection limit of 10 ng mercury. It also suffers from interferences by sulfide and chlorine which must be eliminated by the addition of more reagents.

With the improvement of microwave digestion methods in the past few years, solid sample dissolution has exhibited reduction in decomposition time, reagent volume use, and overall preparation time compared to conventional wet oxidation methods.[6] One major improvement made in the 1980s was in the design of the digestion vessels which caused the advantages of

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pressurized closed-vessel digestions to outweigh the hazards.[7] Since then, many studies have shown that microwave heating of solid samples in closed vessels gives faster and more reliable digestions than parallel hot-plate methods, resulting in more accurate and precise analyte determinations.[8–10] Although laboratory microwave systems with sophisticated computer control are commercially available, they are relatively expensive. However, domestic microwave units have been safely used with little or no modifications for the digestion of various samples.[11–13]

In this paper, a fast and reliable microwave digestion procedure for soil in a pressurized closed vessel with an unmodified domestic microwave oven is presented. Also, the technique of laser-excited atomic fluorescence spectrometry with electrothermal atomization (LEAFS–ETA) is used to determine the amount of mercury in the digested samples. This approach is shown to be more sensitive and selective than the commonly used method of CVAAS.

EXPERIMENTAL

Instrumentation

An unmodified General Electric Model #JES65T domestic microwave oven with 0.017 m^3 cavity space and 10–100% full power (600 W) capability in 10% increments was used for the digestions. The Parr Model #4781 high-pressure microwave acid digestion bomb was used to carry out sample decompositions. This type of vessel consists of a thick-walled inter PTFE sample cup with lid surrounded by a polymeric, microwave-transparent outer casing equipped with four pressure relief ports. It has an upper temperature limit of 250°C, a pressure limit of 1200 psi, and a maximum inorganic loading limit of 1.0 g. A Ziplock plastic bag was used to protect the microwave oven components by containing any corrosive vapors released during the digestion.

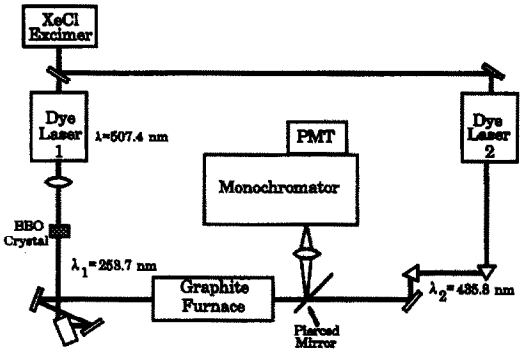

Fig. 1. Schematic instrumentation of LEAFS–ETA system.

The LEAFS-ETA instrumentation is shown in Fig. 1 and consisted of a Lumonics TE-860-4 XeCl excimer pump laser, two Molectron DL-14 tunable dye lasers, BBO frequency doubling crystal, Perkin-Elmer HGA-400 graphite furnace with programmer, SPEX 1680 double monochromator, and Hamamatsu 1P28 photomultiplier tube. Coumarin 500 and 440 laser dyes were used in the first and second tunable dye lasers, respectively. The parameters and conditions for the determinations were: excimer pump laser: frequency, 10 Hz; energy, 70 mJ/pulse; dye laser 1: wavelength output, 507.4 nm; energy, 2.4 mJ/pulse; dye laser 2: wavelength output, 435.8 nm; energy, 1.9 mJ/pulse; BBO doubling crystal: wavelength output, 253.7 nm; optical efficiency, 11%; graphite furnace: tubes, pyrolytically coated; platform, pyrolytically coated; matrix modifier, $PdCl_2$; furnace program, see Table 1.

Reagents

All acid reagents (Fisher Scientific, Orlando, FL, U.S.A.) used were of trace metal certified grade and contained approximately no more than 5 pg/ml (pptr) mercury. All water used for solution preparations was obtained from a laboratory water purification system (Barnstead)

Table 1. Furnace program

Step	Parameter	Temperature (°C)	Ramp time (sec)	Hold time (sec)	Argon flow (ml/min)
1	Matrix modifier dry	110	5	35	300
2	Matrix modifier atomization	1200	0	5	300
3	Sample introduction	20	1	60	300
4	Sample dry	110	5	45	300
5*	Sample atomization	1150	0	5	0
6	Furnace cool	20	1	15	300
7	Clean	2300	1	7	300

*Signal collection step.

having less than 200 ppb of all metal ions. The $PdCl_2$ graphite furnace matrix modifier solution (1000 ppm) was prepared by dissolving 25 mg solid $PdCl_2$ (99.99% purity) in 25 ml of 10% HCl solution. Stock mercury solution (1000 ppm Hg, 1.8% HNO_3, atomic absorption standard) was diluted as needed to prepare standard mercury solutions in approximately the same concentration range as the samples. The microwave digestion reagent was 15.9*M* nitric acid.

National Institute of Standards and Technology (NIST) standard reference material SRM 8406 River Sediment, with a mercury reference content of 60 ng/g, was used. All standard and sample solutions were stored in 30 ml Teflon bottles and analyzed within two weeks of preparation. Fisher brand Redi-Tips trace metal certified pipet tips, which have a maximum mercury content of 0.2 ng per tip, were used in all studies.

Microwave digestion procedure

The microwave digestion procedure was used to decompose approximately 0.25 g of 14 air-dried soil samples and the dried standard reference material. A sample size of 250 mg is recommended[14,15] for the EPA method 245.5. One duplicate sample, spiked sample, and SRM sample were digested and analyzed per day as controls, and a blank was measured before and after each batch (containing no more than 14 samples). The digestion procedure was applied to all samples, blanks, and standard solutions. The blanks represented no more than 200 pg/g of mercury in the samples.

The sample was weighed into the cleaned and dried Teflon sample cup. A 10 ml aliquot of 15.9*M* nitric acid was added to the cup. The lid was fastened and the entire unit was reweighed and then placed in the outer casing assembly and secured.

Because of the small size of the microwave cavity, only two samples were digested simultaneously. The two digestion vessels were placed in a Ziplock plastic bag which was then placed in the microwave oven.

The optimized digestion procedure consisted of heating the two vessels for 5 min at 107.8 W (calibrated Power Level 2). The vessels were then removed from the oven and allowed to cool to room temperature. The inner sample cup assembly was reweighed to ensure that the sample weight had not decreased by more than 1% during digestion.

Each 10 ml digested solution was diluted to 25 ml in a volumetric flask to reduce the total acid percentage to a level that would not degrade the graphite furnace tube.

Determination of mercury by LEAFS–ETA

Calibration. A series of 16 standards and a blank were prepared so that 90 pg or less of mercury was measured. A 10 μl aliquot of the digested solution was injected into the graphite furnace and subjected to the furnace program outlined in Table 1. The two spatially and temporally aligned laser beams entered the graphite furnace and produced the two-step excitation of atomized mercury. The resulting fluorescence at 546.2 nm was collected with the pierced mirror by front-surface illumination and focused into the monochromator where its intensity was then measured by the photomultiplier tube. The signal produced was processed by a boxcar integrator (Stanford Model SR250, Stanford Research Systems, Sunnyvale, CA, U.S.A.) and an analog-to-digital interface (Stanford Model SR245).

Triplicate runs of each solution were obtained, and a calibration curve was generated by plotting the peak area of the signals produced *vs.* the mass of mercury in the sample volumes injected.

Sample analysis. The soil samples, standard reference material, and control samples were analyzed according to the same procedure described above except that a 10 μl aliquot of the digested sample solution was injected into the furnace in place of known amounts of mercury standard solutions. Quantitation of mercury in the samples was obtained using the linear calibration curve. Quantitation of mercury in the SRM 8406 was also performed by the standard additions method.

RESULTS AND DISCUSSION

Optimization of microwave digestion procedure

Before the samples could be digested, the parameters of microwave power and digestion time were optimized. Based on various microwave programs employed in industry and other research laboratories (D. Ryan and G. Walker, personal communications),[16] it was observed that a microwave power between 30 and 100 W per vessel was used to digest soil, sediment, and sludge samples under various conditions. Because a domestic microwave oven with few laboratory-level safety features was used in this

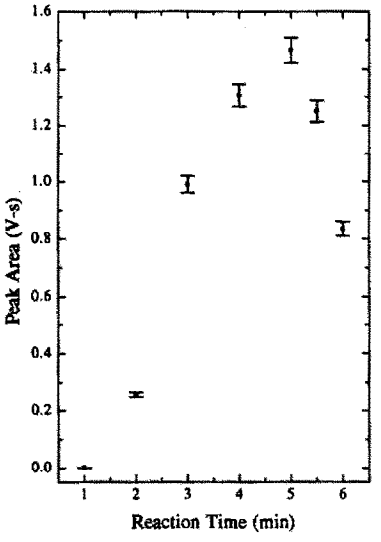

Fig. 2. Optimization of microwave digestion time using two SRM 8406 samples at 53.9 W/vessel.

work, a conservative power of 53.9 W/vessel (corresponding to two vessels heated at calibrated Power Level 2) was used in the heating program. According to Kingston and Jassie,[17] most real samples will decompose if the temperature of the digestion reagent is raised to 175°C and maintained at that level for 5 min. Without temperature feedback sensors in the microwave system, those conditions can only be approximated using the relationship

$$P = \frac{KC_p m \Delta T}{t}, \qquad (1)$$

where P = apparent power absorbed (W), K = conversion factor for calories per second to watts (4.184 J/cal), C_p = heat capacity of reagent (cal.g.$^{-1}$°C^{-1}), m = mass of sample (g), ΔT = final temperature minus initial temperature (°C) and t = time of digestion (sec). Equation (1) can also be mathematically transformed to solve for the final temperature reached for a sample digested at a certain power and time, or for the time of exposure necessary to reach a final temperature. Equation (1), however, is only an approximation of actual conditions because it does not account for deviations due to heat loss or variations in the magnetron output.

Using equation (1) and the digestion procedure outlined in this paper, the temperature of the sample and reagent should reach 175°C in approximately 55 sec. This suggests the final digestion time should be approximately 6 min. Experimentally, this was tested by heating 0.25 g samples of SRM 8406 with 10 ml of nitric acid at Power Level 2 for 1–6 min and then measuring the relative mercury signals obtained with LEAFS–ETA. The results shown in Fig. 2 signify that the optimum digestion time occurred at 5 min. Before 5 min, there was incomplete digestion of the sample, resulting in a low Hg fluorescence signal. After 5 min, slight overpressurization of the vessel caused the volatile mercury to escape, and therefore, the signal decreased. To determine if 5 min digestion time at 53.9 W/vessel was sufficient to leach all the mercury into the sample solution, the standard additions method was used under these conditions to quantify the amount of mercury present in SRM 8406. The concentration of mercury obtained by the LEAFS–ETV method for the SRM 8406 was 58.4 ± 1.8 ng/g dry weight which was in good agreement with the certified value of 60 ng/g.

Sample analysis

Fourteen samples of air-dried soil taken from the Florida Everglades at depths between 0 and 36 cm in 2 cm intervals were digested using the microwave method and were analyzed by LEAFS–ETA. Figure 3 shows typical fluorescence signals from three injections obtained from digested soil samples taken at a core depth of 12–14 cm. The calibration function derived from the linear calibration plot was used to

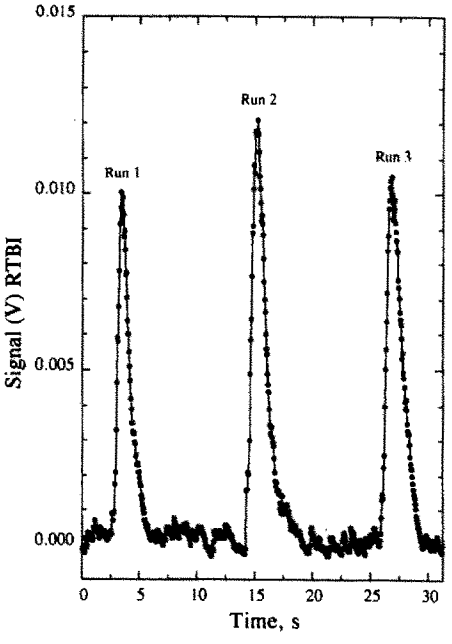

Fig. 3. LEAFS–ETA signal from three injections of digested samples from soil samples (core depth 12–14 cm). Signal magnitude is voltage referred to the boxcar input.

determine the concentration of mercury in the injected sample. This value was then converted into the mercury concentration in the original dry solid sample. The results are summarized in Table 2. The differences between the results obtained by microwave digestion with LEAFS–ETA measurement and EPA Series Method 245.5 digestion with CVAAS measurement cannot be analyzed by Student's *t*-test because the CVAAS used the entire sample in the measurement process; therefore, those values given in Table 2 for CVAAS are for single analysis and do not have any precision values. However, it can be seen that both sets of values are generally in good agreement.

Table 2. Comparison of concentrations* of mercury found in soil samples

Core depth (*cm*)	EPA 245.5 digestion with CVAAS†	Microwave digestion with LEAFS–ETA‡
0–2	312	325 ± 9
4–6	282	294 ± 9
6–8	148	158 ± 5
8–10	129	203 ± 6
10–12	98	104 ± 3
12–14	86	89 ± 3
14–16	69	74 ± 2
16–18	64	68 ± 2
22–24	31	39 ± 1
24–26	16	37 ± 1
26–28	30	33 ± 1
28–30	17	27 ± 0.8
30–32	24	31 ± 1
34–36	40	42 ± 1
22–24(s)§	NR	111 ± 3
30–32(s)§	NR	108 ± 3
SRM 8406‖	NR	58 ± 2

*Concentration in original, solid sample (ng/g).
†Single analysis; previous study (G. Walker, personal communication); NR = not reported.
‡Mean value ± SD, $N = 3$ measurements of the same microwave digested soil sample.
§Sample spiked with 20 ng Hg.
‖Certified value of 60 ng/g.

Figures of merit

The LEAFS–ETA method produced good precision in the determination of mercury in the digested standards and samples; the instrumental precision based on multiple analyses of the same digested solution gave an RSD of 3%. Figure 3 illustrates the typical signals collected for three measurements of one sample.

Based on current EPA criteria, the recovery of mercury from control samples is used as a gauge to measure the performance of a particular method. The per cent recovery of mercury from spiked samples is given by

$$\%\text{Recovery} = \frac{(\text{spiked sample result} - \text{sample result})}{\text{spike added}} \times 100. \quad (2)$$

The digested SRM 8406 is known as the laboratory control solid sample (LCSS), and its per cent recovery is given by

$$\%\text{Recovery} = \frac{\text{measured concentration}}{\text{certified concentration}} \times 100. \quad (3)$$

The EPA's acceptable %Recovery range for these controls is between 75 and 125%, inclusive. In this work, the soil samples taken from core depths of 22–24 cm and 30–32 cm were spiked and analyzed for mercury and produced %Recoveries of 94 and 98%, respectively. The %Recovery of mercury from the SRM 8406 was 99%. These values fell well within the EPA guidelines and indicate that the microwave digestion procedure followed by LEAFS–ETA analysis is a suitable method for the determination of mercury in soil. The discrepancies between the EPA method and the LEAFS–ETA method for 8–10 cm, 24–26 cm, 28–30 cm, and 30–32 cm core depths were most likely a result of sampling errors due to heterogeneities in the sediments for both methods, loss of mercury in the transfer process to the absorption cell in the CVAAS method and/or loss of mercury due to incomplete digestion and possibly contamination of the samples during the EPA digestion procedure.

The concentrational limit of detection (LOD) was calculated at three times the standard deviation of the blank signal divided by the slope of the calibration curve. The absolute detection limit was obtained by multiplying the concentration LOD by the sample volume used in each technique. The concentrational detection limits found in this work were 135 pg/ml and 1 pg/ml for the EPA Method 245.5 CV–AAS and the microwave digestion LEAFS–ETV methods, respectively; the absolute detection limits for the two methods were 7 ng and 14 fg, respectively. It can be seen from Table 3 that microwave

digestion of soil coupled with analysis by LEAFS–ETA has a concentration LOD more than two orders of magnitude lower than the EPA Series Method 245.5 digestion of soil with detection by CVAAS. On an absolute basis, however, the LEAFS–ETA detection with microwave digestion has a limit of detection more than five orders of magnitude lower than that for CVAAS detection with EPA 245.5 digestion.

CONCLUSIONS

The results presented in this work show that the combination of LEAFS–ETA analysis with microwave-assisted sample digestion provides an accurate, reliable, and rapid determination of mercury in soil. The method of laser-excited atomic fluorescence spectrometry combined the selectivity of a two-color excitation process, the sensitivity of fluorescence detection, and the high efficiency of atomization in a graphite tube to produce a highly sensitive technique for the determination of mercury compared to the commonly used method of cold vapor atomic absorption spectrometry. The microwave digestion procedure was a rapid and simple method that decomposed the soil sample in a fraction of the time required by the wet-oxidation method, and the only reagent used was nitric acid. Per cent recovery studies showed that the procedure was reliable and accurate.

Acknowledgements—The authors wish to thank Dr J. Delfino and Dr B. Rood, Department of Environmental Engineering Sciences, University of Florida, for supplying the soil samples and allowing the use of their CVAAS instrumentation. This work was supported by Eastman Kodak Company, Rochester, NY, U.S.A.

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