

# AAS Determination of Total Mercury Content in Environmental Samples

M. MOSKÁLOVÁ and M. ŽEMBERYOVÁ\*

*Department of Analytical Chemistry, Faculty of Natural Sciences,  
Comenius University, SK-842 15 Bratislava*

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Two methods for the determination of total mercury content in environmental samples, soils and sediments, were compared. Dissolution procedure of soils, sediments, and biological material under elevated pressure followed by determination of mercury by cold vapour atomic absorption spectrometry using a MHS-1 system and direct total mercury determination without any chemical pretreatment from solid samples using a Trace Mercury Analyzer TMA-254 were compared. TMA-254 was also applied for the determination of mercury in various further standard reference materials. Good agreement with certified values of environmental reference materials was obtained.

For the determination of the quality and purity of water, food, and other environmental samples, accurate determination of total mercury contents is of basic importance. Numerous methods for the determination of total mercury in environmental samples [1–9, 11], biological materials [10, 11], food [12–14], and clinical samples [15–17] have been described. In the literature different decomposition methods have been presented for which a total mineralization of the sample with a destruction of the organic matter taking into account possible mercury losses, represents an important criterion [18, 19]. In this connection the possibility of a direct mercury determination in solid or liquid environmental samples of different character, without any chemical pretreatment, using the instrument TMA-254 [20] shows considerable advantages.

In the present work a mineralization procedure of soils and sediments and bovine liver at elevated pressure followed by reduction by  $\text{SnCl}_2$  and determination of the total mercury by atomic spectrometry using mercury hydride system MHS-1 [21] is compared with the data on Hg concentration in the same samples determined from solid samples after isolation of mercury on gold amalgamator. The samples need only limited manipulation, no reagents are necessary and so possible contamination from added reagent is eliminated. The accuracy of the determination was checked also on various further certified reference materials.

## EXPERIMENTAL

A 1000  $\mu\text{g dm}^{-3}$  stock standard solution of mercury (Merck) was used. Working standards solu-

tions containing  $w(\text{K}_2\text{Cr}_2\text{O}_7) = 0.005\%$  were prepared freshly every day. All other chemicals as HCl, HF,  $\text{HNO}_3$ ,  $\text{H}_3\text{BO}_3$ , and  $\text{SnCl}_2$  were of analytical grade purity.

Two soil samples from Slovakia, Luvic Stagnosols (WRP 1994) from surroundings of Zvolen town from three horizons: 10–20 cm (ZV-I), 30–40 cm (ZV-II), 50–60 cm (ZV-III) and calcalit Aplic Chernozem (1994) from surroundings of Trnava town from three horizons: 5–15 cm (TT-I), 30–40 cm (TT-II), 70–80 cm (TT-III), were chosen.

NIES No. 2 pond sediment (National Institute for Environmental Studies, Japan Environmental Agency), bovine liver No. 12-2-01 (Czecho-Slovak Metrological Institute), pine needles 1575, tomato leaves 1573 (National Bureau of Standards, USA), kale (Bowen's kale), and IAEA/Soil 7 (International Atomic Energy Agency, Austria) were used as reference materials (RM).

The conditions used for the mercury determination using a single-purpose instrument Trace Mercury Analyzer, TMA-254 (Institute of Chemical Technology, Prague, Czech Republic) designed for the determination of mercury both in solid or liquid samples, were as follows: radiation source low-pressure mercury vapour lamp (wavelength 253.6 nm), time of drying 60 s, drying temperature 110°C, time of decomposition 120 s, decomposition temperature 850°C, carrier gas oxygen (flow rate 160  $\text{cm}^3 \text{min}^{-1}$ ). Optimum analyzable ranges were R1 to 20 ng and R2 to 200 ng of mercury. For mercury determination after dissolution an AAS Perkin—Elmer Model 306 equipped with the apparatus Mercury Hydride System (MHS-1) was

\*The author to whom the correspondence should be addressed.

**Table 1.** Comparison of Total Mercury Determination in Soil Samples and RM of Pond Sediment and Bovine Liver by TMA-254 and MHS-1

Sample	TMA-254		MHS-1	
	$L_{1,2}/(\mu\text{g g}^{-1})$	$s_r/\%$	$L_{1,2}/(\mu\text{g g}^{-1})$	$s_r/\%$
TT-I	0.072 ± 0.002	2.78	0.076 ± 0.003	3.11
TT-II	0.030 ± 0.002	6.67	0.035 ± 0.004	7.89
TT-III	0.027 ± 0.003	7.31	0.030 ± 0.003	9.20
ZV-I	0.110 ± 0.002	1.62	0.123 ± 0.007	5.45
ZV-II	0.060 ± 0.002	3.01	0.072 ± 0.005	6.94
ZV-III	0.056 ± 0.004	2.82	0.069 ± 0.004	5.15
NIES	1.305 ± 0.011	0.47	1.283 ± 0.027	1.30
Bov. liver	0.374 ± 0.009	1.51	0.367 ± 0.012	3.38

Noncertified value of NIES (pond sediment):  $1.300 \mu\text{g g}^{-1}$

Certified value of bovine liver:  $(0.370 \pm 0.020) \mu\text{g g}^{-1}$

used. The conditions used for mercury determination in the electrically heated quartz cuvette of the MHS-1 [21] were as follows: lamp current EDL, power input 5 W, wavelength 253.6 nm, spectral slit width 0.7 nm, temperature of the quartz tube 250 °C, gas argon. Autoclave ZA-1, Zahnašovice (Czech Republic) for dissolution under elevated pressure was used.

### Dissolution Procedure

*Dissolution of soil samples and RM pond sediment:* In the PTFE autoclave vessel sample mass 1 g and 10 cm<sup>3</sup> of acid mixture (38 % HF—65 % HNO<sub>3</sub> ( $\varphi_r = 1:1$ )) were added. The sample was destructed for 6 h in autoclave at 160 °C (in a drying box). To the cool sample 15 cm<sup>3</sup> of saturated H<sub>3</sub>BO<sub>3</sub> solution were added. The solution was set up to 50 cm<sup>3</sup> with redistilled water and filtered. This procedure from literature [22] recommended for soil decomposition was further modified. The sample was not evaporated to dryness after destruction in autoclave (due to potential mercury losses), but saturated H<sub>3</sub>BO<sub>3</sub> was added for HF binding and from this solution mercury was measured.

*Dissolution of bovine liver:* In the PTFE autoclave vessel 0.2 g of sample, 3 cm<sup>3</sup> of 65 % HNO<sub>3</sub>, and 2 cm<sup>3</sup> of redistilled water were added. The sample was destructed for 4 h in autoclave at 140 °C (in a drying box). The cool sample was set up to 50 cm<sup>3</sup> with redistilled water.

### Determination of Total Mercury

Mercury from the solid soil samples, RMs pond sediment, and bovine liver without any chemical pretreatment was determined using TMA-254 instrument after following procedure: 25—30 mg of homogenized soil sample, sediment or bovine liver were weighed on platinum boat, then automatically transferred into a combustion furnace where they were initially dried, then combusted in the stream of oxygen. The com-

bustion products passed through a catalytic furnace where the oxidation was completed. The combustion isolated products were then passed in a stream of oxygen through a gold amalgamator where mercury was trapped quantitatively. After heating of the amalgamator to a high temperature, the entrapped mercury was released and driven to tandem measuring cells where absorbance was measured. The whole analytical run including all the parameters affecting the sensitivity and reproducibility of the determination was controlled by a microprocessor. Calibration was performed using standard solution containing 20 ng of mercury, analyzable range R1.

For the determination of total mercury contents in the same samples after dissolution procedure Cold Vapour AAS (CVAAS) with MHS-1 apparatus was used. To an optimal sample in volume of 20 cm<sup>3</sup> reduction reagent, 2.5 cm<sup>3</sup> of 5 mass % SnCl<sub>2</sub> in 2 vol. % HCl, was added and after reduction mercury was determined in electrically heated quartz cuvette.

## RESULTS AND DISCUSSION

The results of total mercury contents determined by both techniques are compared in Table 1. The confidence interval  $L_{1,2}$  for TMA-254 was calculated according to [23] from the results obtained on six measurements from solid samples. The confidence interval  $L_{1,2}$  for MHS-1 was calculated from the results obtained on six parallel decomposed samples. The confidence intervals and the relative standard deviations were calculated on the significance level  $\alpha = 0.05$ .

The agreement of mercury contents determined using two independent analytical methods under study was tested by Youdenov's graphical method [24] comparing amounts of mercury determined by MHS-1 and TMA-254. The regression equation for mercury reads

$$\text{Hg(MHS-1)} = (1.083 \pm 0.06264)\text{HgTMA-254} \\ + (0.00327 \pm 0.00411)$$

The slope of the regression line can be considered as

**Table 2.** Determination of Total Mercury in Certified Reference Materials

Reference material	TMA-254		Certified values of RM/( $\mu\text{g g}^{-1}$ )
	$L_{1,2}/(\mu\text{g g}^{-1})$	$s_r/\%$	
Pine needles	$0.146 \pm 0.016$	5.99	$0.150 \pm 0.050$
Tomato leaves	$0.086 \pm 0.011$	6.77	0.100 *
Kale	$0.173 \pm 0.009$	2.39	$0.171 \pm 0.028$
IAEA/Soil 7	$0.007 \pm 0.001$	15.05	$0.003-0.07$ *

\* Noncertified value.

equal to one and the intersection on the  $y$  axis as equal to zero. The two methods thus give identical results for the determination of Hg.

The higher results in upper horizon in both cases of agricultural soils are caused by application of fertilizers and Hg-containing fungicides that may have increased mercury contents.

Using TMA-254 further reference materials were measured and the results were compared with certified values. The results are presented in Table 2. The confidence interval  $L_{1,2}$  for the standard reference materials was calculated according to [23] from the results obtained for six measurements. The confidence interval and the relative standard deviations were calculated on the significance level  $\alpha = 0.05$ . The detection limit for TMA-254, 0.15 ng was computed from confidence band according to Ref. [25] by program Adstat ver.1.2 (TriloByte Ltd., Pardubice, Czech Republic).

Determined amounts of mercury after dissolution procedure of soil and sediment samples as well as bovine liver were compared with the contents of mercury determined directly from the solid samples. The contents of mercury determined in various further reference materials using TMA-254 were statistically identical with corresponding certified values. TMA, being less tedious and time-consuming of both, gives statistically identical results with well established CVAAS method. This method is rapid and free of the contamination from the reagent used for the dissolution of the samples.

The procedure is very useful for monitoring of the extent of contamination with mercury in environmental samples.

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