Single-Purpose Atomic Absorption Spectrometer AMA-254 for Mercury Determination and its Performance in Analysis of Agricultural and Environmental Materials

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A single-purpose atomic absorption spectrometer based on *in situ* dry ashing followed by gold amalgamation cold vapour AAS was evaluated. Various agricultural and environmental certified reference materials (CRMs) and internal reference materials of wide range of mercury contents were analyzed and good agreement with certified values was found. Control chart of the results of mercury determination in CRM 12-02-03 (Lucerne) as well as the results of interlaboratory trials suggested that the system of mercury determination was under control. Evidently, wide spectrum of agricultural and environmental materials can be analyzed for mercury contents even at levels less than 1 μg kg^{-1}.

Mercury and its compounds belong to the most dangerous contaminants of the environment. Biota can be exposed to mercury from a variety of environmental sources such as mine tailings, industrial effluent, agricultural drainwater, and atmospheric deposition from electric power generation. Bioaccumulation of both inorganic and methylated compounds of mercury in food chain results in mercury toxicoses at high trophic level feeders. Recently, the newest pieces of information concerning toxicity of Hg to wildlife, the mechanisms of Hg toxicity, and the measurement of Hg in biota samples were reviewed [1, 2].

The cold vapour AAS method (CVAAS) is one of the most widely used techniques for determination of trace amounts of total mercury in biological and environmental materials [3, 4]. For Hg contents lower than 0.1 mg kg^{-1} it is necessary to use additional steps in the CVAAS procedure which include preconcentration of Hg by amalgamation on gold [5—8] or silver [9] traps to increase mercury concentration and to avoid interferences occurring in case residual organic matrix remains in sample solution. Various commercial systems based on gold amalgamation CVAAS for mercury determination in sample solution were recently designed, *e.g.* by *Moffett* [10], *Urba et al.* [11], and *Livardjani et al.* [12].

For several matrices, the cold vapour technique can be used directly, without the need of previous decomposition (urine, blood, saliva [13]). Rarely, slurry sampling of coal fly ash [14] or plant and animal materials [15] was applied for mercury determination by either CVAAS or cold vapour generation followed by mercury trapping, preconcentration, and atomization in Ir-treated electrothermally heated graphite atomizer. However, for most biological matrices, mercury must be separated from the matrix before determination. This step is extremely difficult. Only a complete wet ashing (*e.g.* in the mixture of HNO_3 + H_2SO_4) leads to accurate results [3]. When the digestion is incomplete, volatile organic compounds can also give an analytical signal resulting in too high values for the mercury contents [16].

At the ultratrace level, contamination-free digestion for the subsequent mercury determination is possible in quartz vessels with HNO_3 + $HClO_4$ mixture. Very low mercury contents require specially purified acids [17]. Generally, wet decomposition methods are performed under atmospheric or increased pressure with both conventional [6, 17—19] and microwave [20, 21] heating sources. The fully automated system based on microwave digestion system coupled on-line with flow injection CVAAS was described resulting in simplification of the procedure as well as in reduction of the secondary contamination, and improvement of analytical quality of the results [22, 23]. Rarely, dry combustion of the sample in pressurized oxygen bomb [24] is recommended as possible decomposition method. *Koops et al.* [25] described decomposition of pelletized samples of milk powder with pure oxygen in a small burning quartz chamber (Trace-O-Mat). Low-temperature ashing (LTA) was applied as sample pretreatment before microwave acid digestion of coal samples as well. However, about 18 % of total Hg was lost during the LTA pretreatment [26].

Since 1986, the special single-purpose atomic absorption spectrometer called Trace Mercury Analyzer

TMA-254 has been used in majority of Czech and Slovak analytical laboratories. This device is based on the unique concept of *in situ* dry decomposition of liquid or solid sample (maximally 300 mg) in a stream of oxygen and passage of the combustion gases through the catalytic column, followed by trapping Hg on the gold amalgamator. Heating the amalgamator rapidly evaporates preconcentrated mercury which is then transported into the system of measuring cells, and its atomic absorption is measured. The whole analysis is performed automatically without the need of preliminary dissolution and/or decomposition of the sample [27]. However, interferences connected with an incomplete decomposition procedure – caused by the decreased activity of the aged catalyst – were observed for mercury determination in bovine liver when TMA-254 was used. The deterioration of the catalyst resulted in somewhat higher values of mercury content found in RM 12-02-01 Bovine Liver (7.5 %) when compared to certified value [28].

In 1992, the second generation of this instrument, called Advanced Mercury Analyzer AMA-254, was introduced. In comparison with TMA-254, the electronic part is completely re-designed; the IBM-compatible PC with the special software controls AMA-254. The mechanical, optical, and chemical parts were improved, too. All the changes resulted in better sensitivity (improved by about one order of magnitude, to detection limit 0.01 ng Hg; working range is 0.05 to 500 ng Hg), better reproducibility (< 1.5 %), and much better overall reliability of operation [29]. The results of mercury determination in soil samples by AMA-254 suggested good agreement with conventional CVAAS as well as with certified values of reference materials [30]. Regardless of several instruments based on similar principle developed in the last decade including some commercially available devices [9, 31, 32], AMA-254 represents dominant technique used for mercury determination in majority of Czech and Slovak analytical laboratories.

EXPERIMENTAL

The following CRMs were analyzed in this study: plant materials RM 12-02-03 Lucerne, SRM NIST 1572 Citrus Leaves, and BCR-62 Olive Leaves; animal materials ARC/CL Milk Powder, BCR-184 Bovine Muscle, SRM NIST 1577a Bovine Liver, and RM 12-02-01 Bovine Liver; environmental materials SO-3 Soil and BCR-144 Sewage Sludge. Certified mercury contents are listed in Table 1.

Set of internal reference materials (IRMs) analyzed in the framework of International Plant-Analytical Exchange [33, 34] organized by WEPAL, Wageningen (The Netherlands) is listed in Table 2. Data obtained within this test are characterized by median and median of absolute deviations (MAD). *Z*-Scores were applied for the accuracy evaluation using the following formula

$$Z = \frac{Y - Y_{\mathrm{M}}}{\mathrm{MAD}}$$

where Y_{M} is median of IPE values.

The usual way of the *Z*-score classification as $|Z| \leq 2$ – satisfactory, $2 < |Z| < 3$ – questionable, and $|Z| \geq 3$ – unsatisfactory was used in the evaluation of the data obtained.

The above set of CRMs and IRMs was analyzed for mercury contents using AMA-254 (Altec, Czech Republic) under the following conditions: typical sample mass 50 mg, drying time 10 s, decomposition time 150 s, waiting time (necessary for quantitative trapping of released mercury on the gold amalgamator) 45 s. The same conditions were applied for mercury determinations using TMA-254 (Prague University of Chemical Technology Workshops, Czech Republic). All the measurements were done with a fresh catalyst in the catalytic furnace. Wilcoxon's nonparametric test was applied for the comparison of the analytical data obtained by both AMA and TMA instruments with certified values.

In addition, control chart of mercury contents found in RM 12-02-03 Lucerne analyzed in our laboratory regularly simultaneously with routine samples as quality assurance was evaluated.

An independent analysis of SRM NIST 1577a Bovine Liver was done by neutron activation analysis (NAA); *Kučera* and *Soukal* [35] described detailed procedure.

RESULTS AND DISCUSSION

Accuracy Evaluation

The results obtained compared to certified values of mercury in CRMs are summarized in Table 1. For CRMs SO-3 Soil, RM 12-02-03 Lucerne, BCR-62 Olive Leaves, and RM 12-02-01 Bovine Liver there is a good agreement of the AMA results with both TMA results and the certified values. No significant differences were found at the significance level $p < 0.05$ in all the cases.

For SRM NIST 1572 Citrus Leaves, significantly lower values were obtained with TMA as compared to both AMA and the certified value. However, the result is within the confidence interval for this material ($\Delta w(\mathrm{Hg}) = 0.02\ \mathrm{mg\ kg^{-1}}$) and taking into account the relatively low sample mass applied (50 mg) the result can be considered as acceptable.

On the contrary, a significantly higher value was obtained for CRM BCR-144 Sewage Sludge with TMA as compared to both AMA and the certified value. This result suggested the insufficient efficiency of the catalyst in TMA for such matrices as sewage sludge. Also, an improved quality of the catalyst in AMA leads to the complete decomposition of the complex sludge matrix.

Table 1. Results of Mercury Determination in Various CRMs by TMA-254 and AMA-254 (w(Hg, of dry matter)/(mg kg^{-1}))

CRM	Certif. value	n	TMA-254		AMA-254	
			Mean	SD^b	Mean	SD
BCR-184 Bovine Muscle	0.0026	6	0.004	0.001	0.0023	0.0011
SRM NIST 1577a Bovine Liver	0.004	6	0.050	0.027	0.041	0.005
SO-3 Soil	0.017	6	0.014	0.002	0.016	0.001
RM 12-02-03 Lucerne	0.028^a	6	0.026	0.005	0.027	0.007
SRM NIST 1572 Citrus Leaves	0.080	6	0.065	0.009	0.080	0.006
BCR-62 Olive Leaves	0.280	6	0.288	0.013	0.282	0.024
RM 12-02-01 Bovine Liver	0.370	6	0.372	0.055	0.370	0.014
BCR-144 Sewage Sludge	1.46	6	1.71	0.19	1.33	0.01

a) Information value only, *b*) standard deviation.

Table 2. Results of Mercury Determination in Plant Materials from IPE WEPAL Interlaboratory Test

Sample	Material	w(found) / μg kg^{-1}	w(median) / μg kg^{-1}	MAD / μg kg^{-1}	Z-Score
100	Grass (GR94)	10.2	10.3	0.68	−0.21
119	Rosa (plant)	8.7	7.36	0.44	1.77
129	Coconut (fibre)	7.8	8.05	0.71	−0.46
148	Lucerne-91	8.1	8.4	0.5	−0.34
156	Oak leaf	87	87	6.6	0.08
949	Aubergine (plant)	3.8	3.83	0.3	0.02
100	Grass (GR94)	10.8	10.6	0.4	0.45
683	Oats (straw)	19.4	19	1.7	−0.13
149	Lucerne-92	7.47	8.3	1.17	−0.57
100	Grass (GR94)	9.8	11	0.7	−1.71
950	Melon	58.6	59.1	3.12	−0.14
151	Grass (95)	7.65	8.75	0.45	−1.37
949	Aubergine (plant)	4.28	4.02	0.27	0.52
157	Beech (leaf)	101	84.7	8.55	1.37
885	Maize	10.7	10	0.89	0.61
100	Grass (GR94)	10.2	10.1	1.1	0.16
883	Carnation (straw)	55.3	57	4.5	−0.7
141	Tym	66	73	4.45	−0.86
100	Grass (GR94)	9.5	10.9	0.35	−2.12
132	Broccoli	11.1	12.6	1.61	−0.48
100	Grass (GR94)	9.6	10.6	0.8	−0.89
939	Lucerne	14.3	14.5	1.65	−0.22
950	Melon	57.5	62	4.35	−0.96
126	Maize (plant)	4.2	5.49	0.7	−1.13
952	Grass (mixture)	33.2	35.5	2.25	−0.61
100	Grass (GR94)	10	10.6	0.6	−0.66
136	Bokashi	6.81	5.1	0.9	1.18
883	Carnation (straw)	56.4	54.7	2.3	0.29

In the case of SRM NIST 1577a Bovine Liver, no accurate either AMA or TMA results were found; both methods gave results, which were significantly higher than certified value. However, the elevated value was confirmed by an independent method (NAA); it is probably due to secondary contamination of the bottle of reference material used in this study. This bottle was previously used for analyses with lower requirement for clean laboratory environment.

For the material with the lowest mercury content of the CRMs, *i.e.* BCR-184 Bovine Muscle, higher result than certified value was obtained by TMA. This could be a consequence of contamination of an empty sample boat and/or laboratory environment. In case of AMA, the automatic blank correction together with increased sensitivity of the measurement allowed accurate determination of mercury.

The capacity of the AMA instrument to determine extremely low mercury levels can be demonstrated with CRM ARC/CL Milk Powder. During the certification process of this material [36], mercury levels obtained were always under the detection limit of the methods used within the interlaboratory test (0.001 mg kg^{-1}). In our case, the mercury content determined by AMA in this material after five-fold enrichment of mercury on gold amalgamator (total mass of

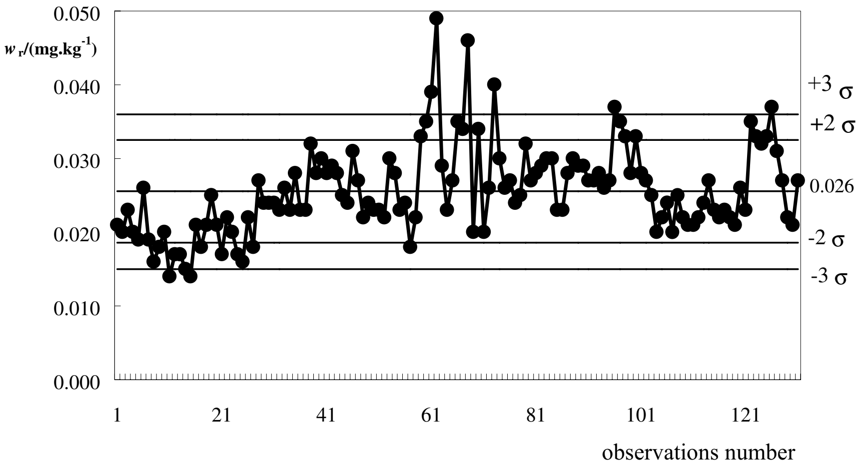

Fig. 1. Control chart of mercury content in RM 12-02-03 Lucerne determined by TMA-254.

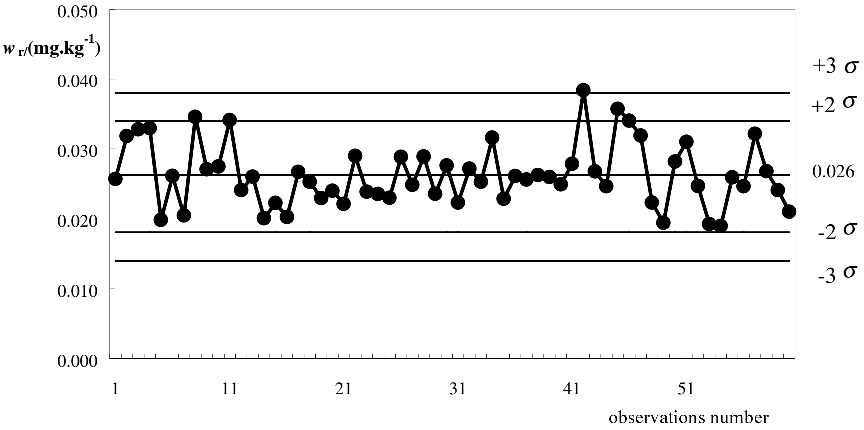

Fig. 2. Control chart of mercury content in RM 12-02-03 Lucerne determined by AMA-254.

sample 500 mg) was (0.00022 ± 0.00009) mg kg^{-1}. Detection limit given as treble standard deviation of mercury content in blank samples was 0.00011 mg kg^{-1}.

Generally, for all the CRMs followed, accurate results were obtained by means of AMA-254; and the instrument can perform well within the range of mercury contents between 0.0026 mg kg^{-1} and 1.46 mg kg^{-1} for various biological and environmental matrices.

Interlaboratory Trials

The results of mercury determination in 22 IRMs of plant origin obtained using AMA-254 in the frame of International Plant-Analytical Exchange [33, 34] are summarized in Table 2. The set of samples represented various plant species or plant tissues of agricultural crops. Mercury contents in these materials were usually very low with median level not exceeding 100 μg kg^{-1}. The results measured are compared with median of the results obtained within the interlaboratory test *via* *Z*-score value. With one exception of grass sample No. 100, the *Z*-scores did not exceed the limit for satisfactory result ($|Z| \leq 2$). The measured mercury contents in periodically repeated sample of grass (No. 100) confirmed fairly good repeatability of the results. Thus, the applicability of the AMA-254 instrument for mercury determination in various types of agricultural materials including the samples containing low level of mercury was confirmed.

Long-Term Stability of the Analytical System

To evaluate a long-term behaviour of an analytical system of mercury determination, control charts of found Hg contents were obtained by analyzing of RM 12-02-03 Lucerne (information mercury value 0.028 mg kg^{-1}). As can be seen in Figs. 1 and 2, laboratory mean of the Hg content determined by the TMA device (0.026 mg kg^{-1}, Fig. 1) is comparable with the laboratory mean determined by AMA (0.026 mg kg^{-1}, Fig. 2) and both means agreed well with the information value. The upper and lower critical limits are comparable for both control charts. However, in the case of TMA, nine results (*i.e.* 7 %) were out of control limits (3 σ) while all the AMA results fell within the limits. If the control limits were stated at the level representing 2 σ, 5 % of AMA data and even 23 % of TMA data were out of these limits.

The results suggested that mechanical, optical, and chemical improvements in the construction of the AMA device led to better stability of the analytical system of mercury determination as compared to previous version of the device (TMA). Comparing both versions of analytical instruments, analytical conditions, duration of the analytical procedure as well as measurement costs are comparable for both versions of the instrument. However, improvements of the capacity of the catalyst of AMA instrument lead to the reduction of interferences resulting in enhanced precision, accuracy, and long-term stability of the analytical results.

Results evaluated in this study suggest that an application of an advanced version of the single-purpose atomic absorption spectrometer (AMA-254) for total mercury determination leads to reliable results with various biological and environmental matrices over a wide content range. Analytical system of mercury determination using this device can be under control for a long time. Evidently, this method is suitable for easy, fast, precise, and accurate determination of mercury in wide scale of agricultural and environmental materials resulting in reasonable evaluation of mercury pollution of the environment.

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REFERENCES

1. Wolfe, M. F., Schwarzbach, S., and Sulaiman, R. A., *Environ. Toxicol. Chem. 17*, 146 (1998).
2. Boening, D. W., *Chemosphere 40*, 1335 (2000).
3. Clevenger, W. L., Smith, B. W., and Winefordner, J. D., *Crit. Rev. Anal. Chem. 27*, 1 (1997).
4. Yan, X. P. and Ni, Z. M., *Anal. Chim. Acta 291*, 89 (1994).
5. Welz, B. and Schubert-Jacobs, M., *Fresenius Z. Anal. Chem. 331*, 324 (1988).
6. Vermeir, G., Vandercasteele, C., Temmermann, E., Dams, R., and Versieck, J., *Mikrochim. Acta* (Wien) *3*, 305 (1988).
7. Vermeir, G., Vandercasteele, C., and Dams, R., *Anal. Chim. Acta 220*, 257 (1989).
8. Horvat, M., Lupsina, V., and Pihlar, B., *Anal. Chim. Acta 243*, 71 (1991).
9. Brandvold, D. K., Martinez, P., and Matlock, C., *Anal. Instrum. 21*, 63 (1993).
10. Moffett, J. H., *Varian Instruments at Work AA-104*, p. 1. Varian Inc., 1991.
11. Urba, A., Kvietkus, K., Sakalys, J., Xiao, Z., and Lindquist, O., *Water, Air, Soil Pollut. 80*, 1305 (1995).
12. Livardjani, F., Heimburger, R., Leroy, M. J. F., Jaeger, A., and Lugnier, A. A., *Analusis 23*, 392 (1995).
13. Ngim, C. H., Foo, S. C., and Phoon, W. O., *J. Anal. Toxicol. 12*, 132 (1988).
14. Moreda-Pineiro, J., Lopez-Mahia, P., Muniategui-Lorenzo, S., Fernandez-Fernandez, E., and Prada-Rodriguez, D., *Spectrochim. Acta, Part B 57*, 883 (2002).
15. Rio-Segade, S. and Bendicho, C., *J. Anal. At. Spectrom. 14*, 1907 (1999).
16. Coles, L. E., Guthenberg, H., Kato, T., and Kojima, K., *Pure Appl. Chem. 57*, 1507 (1985).
17. May, K. and Stoeppler, M., *Fresenius Z. Anal. Chem. 317*, 248 (1984).
18. Salisbury, C. D. and Chan, W., *J. Assoc. Off. Anal. Chem. 68*, 218 (1985).
19. Landi, S., Fagioli, F., and Locatelli, C., *J. AOAC Int. 75*, 1023 (1992).
20. Lippo, H., Jauhiainen, T., and Peramaki, P., *At. Spectrosc. 18*, 102 (1997).
21. Julshamn, K. and Brenna, J., *J. AOAC Int. 85*, 626 (2002).
22. Hanna, C. P. and McIntosh, S. A., *At. Spectrosc. 16*, 106 (1995).
23. Noh, M. F. M., Abd Hamid, T., and Ismail, Z., *At. Spectrosc. 19*, 95 (1998).
24. Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry.* International Textbook Company, London, 1979.
25. Koops, J., deGraaf, C., and Westerbeek, D., *Neth. Milk Dairy J. 38*, 223 (1984).
26. Moreda-Pineiro, J., Beceiro-Gonzalez, E., Alonso-Rodriguez, E., Gonzalez-Soto, E., Lopez-Mahia, P., Muniategui-Lorenzo, S., and Prada-Rodriguez, D., *At. Spectrosc. 22*, 422 (2001).
27. Hlaváč, R., Doležal, J., Kolihová, D., Sychra, V., Pietroš, L., Valenta, S., Püschel, P., and Formánek, Z., *Proc. XXIV CSI*, Garmisch-Partenkirchen, September 1985.
28. Miholová, D., Mader, P., Száková, J., Slámová, A., and Svatoš, Z., *Fresenius' J. Anal. Chem. 345*, 256 (1993).
29. Anonymous, *AMA-254 Advanced Mercury Analyzer.* Altec, Prague, Czech Republic, 1992.
30. Duran, A. C. and Adams, M., *Interciencia 27*, 191 (2002).
31. Chen, B., Wang, X. R., and Lee, F. S. C., *Anal. Chim. Acta 447*, 161 (2001).
32. Cizdziel, J. V., Hinners, T. A., and Heithmar, E. M., *Water, Air, Soil Pollut. 135*, 355 (2002).
33. IPE 2001: Quarterly Reports 2001.1—2001.4, Wageningen Evaluating Programmes for Analytical Laboratories. Environmental Sciences, Wageningen University, Wageningen, The Netherlands, 2001.
34. IPE 2002: Quarterly Reports 2002.1—2002.3, Wageningen Evaluating Programmes for Analytical Laboratories. Environmental Sciences, Wageningen University, Wageningen, The Netherlands, 2002.
35. Kučera, J. and Soukal, L., *J. Radioanal. Nucl. Chem. Articles 168*, 185 (1993).
36. Kumpulainen, J., Paaki, M., and Tahvonen, R., *Fresenius' J. Anal. Chem. 338*, 423 (1990).