ISSN: 0001-5113
AADRAY

ACTA ADRIAT.
33 (1/2): 199-207, 1992

UDC: 546.49 : 543.3 (26)
Original scientific paper

Determination of mercury using the Jerome m-511 Gold Film Mercury Analyzer

Mirjana ŠKREBLIN and Anthony R. BYRNE

"J. Stefan" Institute, University of Ljubljana, Ljubljana, Slovenia

The M-511 Gold Film Mercury Analyzer, manufactured by the Jerome Instrument Corporation, uses a thin gold film as a detector which in the presence of Hg vapour undergoes a proportional increase in electrical resistance. In working with the M-511, besides the method and equipment recommended by the manufacturer, some modifications were introduced, which were shown to improve the original method. Different techniques were used for calibration as well as for measurement of samples: the reduction - aeration method and the Hg vapour injection technique, directly or in combination with a preamalgamation step on a Au-absorber.

Good linearity was obtained for both methods in the examined range between 5-40 ng Hg. Precision is dependent on the mass of mercury; it is 6-10% for quantities greater than 20 ng Hg. The sensitivity of the M-511 was observed to vary within the day and from day to day. Also, it was shown that the sensitivity of the whole procedure in the mercury determination depends greatly on the technique applied.

The applicability of the M-511 for measurement of natural samples was tested by using different reference materials. Results obtained showed that positive interferences were often present (probably caused by acidic fumes or some volatile substances which are liberated from the digested solution during the reduction-aeration step).In some cases it can be overcome by using a preamalgamation step, or by introducing a filter trap for volatile substances. On the basis of our results, supposing that the performance of our M-511 is typical, it seems doubtful if conditions can be found in which reliable determination of real samples can be combined with the originally intended simplicity of measurement of the M-511.

INTRODUCTION

Mercury is known to be one of the most dangerous pollutants and monitoring of its concentrations in the environment is an essential part of the UNEP MED POL Programme; consequently many laboratories need a simple, rapid and inexpensive instrument for its routine determination in various types of environmental samples. Recently, the Jerome Instrument Corporation (JIC) produced the Gold Film Mercury Analyzer, M-511, a new improved version in the line of JIC mercury analyzers which use their patented Gold Film Sensor developed by MCNERNEY *et al.* (1972). Earlier models (M-301, M-411) were preferentialy used for determination of mercury in atmospheric samples (SCHROEDER, 1987), while the M-511, accord-

ing to the manufacturer, can be applicable for analysis of mercury in various environmental samples (sediment, biological material etc.). This portable instrument, which detects mercury at ng levels, is based on the proportional resistance increase of a thin gold film as it becomes amalgamated in the presence of mercury vapour. The instrument is equipped with a microprocessor, internal pump, standard filters and reduction vessel (V=40 ml). This paper describes a series of experiments we performed to test the applicability of the M-511 to different sample types.

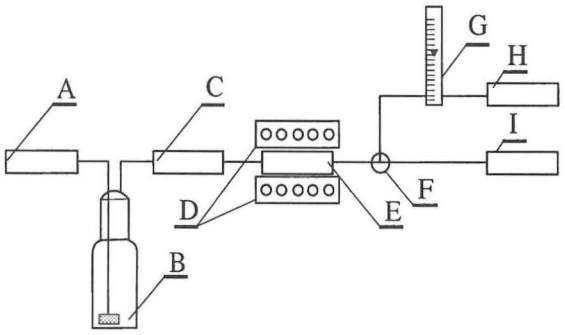

Fig. 1. Diagram of apparatus for determination of mercury by preamalgamation step. (A) activated carbon trap (B) reduction vessel with frit (C) acidic gas filter (D) furnace (E) gold trap (F) three-way tap (G) flow meter (H) water pump (I) M-511

MATERIAL AND METHODS

Prior to the application of the M-511 for analysis of environmental samples, we tested its linearity and reproducibility when working with pure mercury standard solutions and elemental mercury vapour. Calibration and sample measurement procedures were carried out as described below.

I) CALIBRATION PROCEDURE

I-A) **Direct aeration-reduction method**

1) *Procedure recommended by the manufacturer*

All reagents were analytical grade (Merck p.a.). Stock mercury solution: 1 ug Hg/ml in 5% HNO3. Working mercury standards were prepared daily. Reducing agent: 10% $SnCl_2$ in HCl (2 ml conc. HCL + 28 ml redistilled water). An appropriate aliquot of mercury standard was pipetted into a 30 ml glass test tube, then 4 ml conc. HNO3 was added and allowed to stand for 5 minutes. After that redistilled water was added to fill the test tube completely. The solution was transferred into the JIC reduction vessel and after the injection of 1 ml 10% $SnCl_2$, the operation cycle was started. Prior to the next determination, the reaction vessel should be rinsed several times with water to remove the residues of $SnCl_2$. The results obtained are presented in Table 1.

Table 1. Determination of mèrcury from standard solutions using the original procedure (I-A-I)

ng Hg added	5	10	20
mean response	0.8	5.5	11.7
of n measurements	5	10	10
standard deviation	± 0.8	± 1.0	± 0.8
coef. variation (%)	100	18	7

2) *Modified procedure: reversed addition of reactants, modified reduction vessel*

Relatively low and irreproducible responses obtained on using the original procedure (Table 1), which could be caused by the loss of mercury during transfer of solutions or by residues of $SnCl_2$ in the reduction vessel (which are difficult to eliminate completely), as well as the rather complicated procedure, led us to reverse the original procedure and inject mercury ions directly into the JIC reaction vessel already containing 1% $SnCl_2$ in 3 M H_2SO_4 (H_2SO_4 was used instead of HCl because of its higher boiling point to diminish the risk of carry-over of acidic fumes). Using this simplified and improved procedure we tested the reproducibility and linearity of the M-511, as well as its sensitivity to different volumes in the JIC reduction vessel. Results obtained are presented in Table 2 and Fig. 2A. Working with the original JIC reduction vessel we observed that efficiency of removal of mercury from solution

Table 2. Determination of mercury from standard solutions using a modified procedure (I-A-2). Mean values with standard deviations of ten replicate measurement and coefficients of variation are presented.

Volume (ml)	Added mercury	5 ng	10 ng	20 ng	30 ng	40 ng
5	x ± σ	3.3 ± 0.7	8.3 ± 0.7	18.2 ± 0.9	28.5 ± 1.1	3.6 ± 2.1
	var %	21	8.4	4.9	3.8	5.7
10	x ± σ	2.3 ± 0.7	6.8 ± 0.6	15.8 ± 1.2	23.8 ± 1.8	33.0 ± 1.2
	var %	30	8.8	7.6	7.6	3.6
20	x ± σ	2.7 ± 0.7	6.6 ± 0.8	16.4 ± 1.5	25.2 ± 1.5	33.5 ± 1.9
	var %	26	12	9.1	6.0	5.4
30	x ± σ	2.5 ± 1.3	7.4 ± 0.8	16.4 ± 1.2	22.4 ± 1.2	36.2 ± 1.8
	var %	50	11	7.3	5.4	5.0

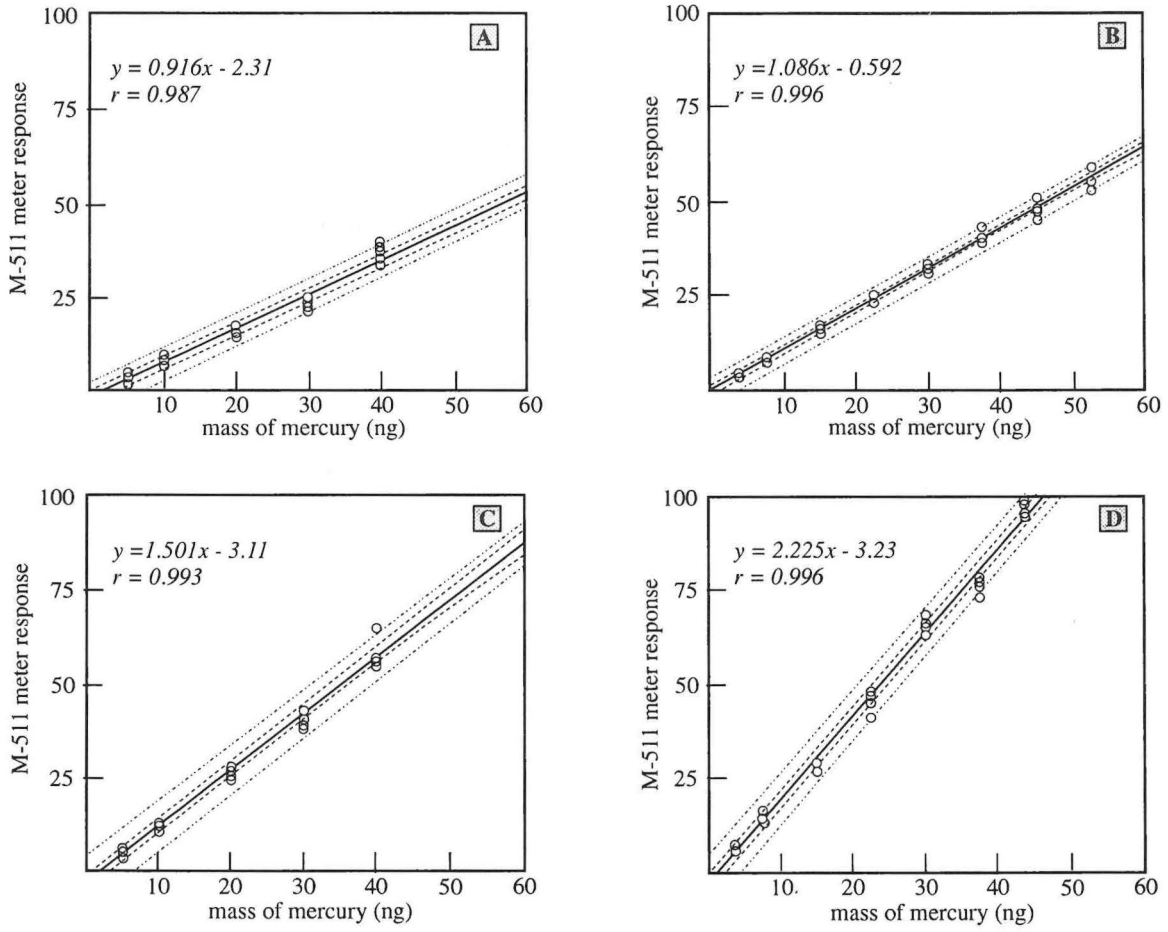

Fig. 2. Comparison of calibration curves, obtained by different methods, for M-511. (a) direct: reduction-aeration (b) direct: vapour-injection (c) preamalgamation: reduction-aeration (d) preamalgamation: vapour-injection. Confidence (– –) and prediction (.....) limits are calculated at 95% level, using Statgraphics computer package.

was not satisfactory for volumes greater than 10 ml, so at least two operation cycles had to be activated to obtain quantitative registration of mercury (until the result displayed was zero). Two replicate measurements of the same sample take 8-12 minutes. This was improved by using another type of reduction vessel with a bubbler made of sintered glass which enabled complete recovery of mercury in on aeration cycle even for a 50 ml volume. Using this ves-

sel, we tested within-day variation of sensitivity, checking instrument responses for 10 ug Hg within 5 hours (Tab. 3).

Table 3. Within - day variations of sensitivity of M-511. Total of 24 successive measurements of a standard solution containing 10 ng Hg f were grouped and mean values of four measurements are presented.

n	mean ± stand. dev.	variation %
1 – 4	6.0 ± 0.8	13.0
5 –8	7.3 ± 0.5	6.8
9 – 12	8.5 ± 0.6	7.0
13 – 16	9.0 ± 0.8	8.8
17 – 20	8.8 ± 0.9	10.2
21 – 24	9.8 ± 0.9	9.2
1 – 24	8.2 ± 1.4	17.0

I-B) **Direct Hg vapour injection method**

Calibration with mercury vapour recommended by DUMMAREY *et al.* (1986) as a fast, precise, accurate method which is free from contamination and matrix effects. Using a precise gas syringe, we injected a known amount of mercury vapour taken from an equilibrated vessel connected to the M-511, immediately after activation of its measurement cycle. The calibration curve is presented in Fig. 2B.

I-C) **Calibration by means of a preamalgamation step**

As will be described later, in working with wet digested natural samples we found serious interferences when direct measurement was applied. In an effort to overcome this problem, we introduced a modified method with a preamalgamation step which is schematicaly shown in Fig. 1. Mercury vapour released from solution (when using the reduction-aeration method), of introduced into the reduction vessel by gas syringe, was drawn by means of a water pump at a flow rate of 40 1/h through a three-way tap to a gold trap in a 4-min amalgamation step and then released from it by heating the furnace at 600°C. Before the deamalgamation step started, the three-way tap was directed to the M-511 which had already been activated. Calibration curves obtained using this preamalgamation reduction-aeration method and the preamalgamation Hg vapour injection method are presented in Fig. 2C and 2D.

II) MEASUREMENT OF SAMPLES

To evaluate the applicability of the M-511 for determination of mercury in natural samples, we carried out a series of experiments using various types of environmental and reference materials, and different methods for sample preparation and measurement. The experiments (coded by capital letters) are described below and surveyed in Table 4., which also presents results obtained by the M-511 in comparison to certified values or to values determined by the CVAAS method which is in routine use in our laboratory (HORVAT *et al.*, 1986).

Experiment A

Sample: mercury polluted sea water 50 ml of preacidified unfiltered sea water (sampled from a heavily polluted area) was analysed by the direct reduction-aeration method, using a 250 ml reduction vessel with a sintered glass bubbler. 1 ml 1% $SnCl_2$ in 3M H_2SO_4 was added as reducing agent.

Experiments B, C, D, E

Samples: Tuna Homogenate; NBS SRM 1566 - Oyster Tissue; IAEA MA-A-2 Fish Homogenate; NBS SRM 1572 - Citrus Leaves

Decomposition of samples (~ 0.5 g) was performed with conc. HNO_3 (4 ml) or $HNO_3/HClO_4$ (4 : 1) under pressure in a PTFE bomb for six hours at 100-110°C. The digested solution was transferred to a 25 ml or 50 ml volumetric flask and diluted to volume with redistilled water. The measurements were made using both direct and preamalgamation reduction-aeration methods.

Experiments F, G

Samples: NBS SRM 1633 a - Coal Fly Ash; NBS SRM 1645 - River Sediment

Decomposition of samples was performed according to MUDROCH *et al.* (1987). The sa-

mple was weighed (0.5 - 1.0 g) into an Erlenmeyer flask, 20 ml conc. HNO_3 was added followed by 1 ml conc. HCl and 20 ml redistilled water. Samples were digested 90 min at 90°C. The digested solution was filtered into a 50 ml calibrated flask and diluted to the mark with redistilled water.

range of mercury additions. The desirable mass of mercury in an aliquot of solution analysed should be in the range of 20-40 ng Hg for optimal precision. This demands a greater sample size for low-level mercury samples and also reduces the number of measurements which can be performed before saturation of the

Table 4. Determination of Hg in various samples using different decomposition and measurement methods.

Experiment	Sample type	Decomposition	M-511 measurement	(n)	M-511 results	CVAAS	Certified values	Remarks
A	highly 1 polluted 2 sea water 3	unfiltered acidified	direct aeration reduction	(2) (2) (2)	1040 (ng/l) 500 (ng/l) 870 (ng/l)	1080 (ng/l) 520 (ng/l) 900 (ng/l)		Comment 1)
B	Tuna homogenate	PTFE bomb HNO_3, 100-110°C 6 hours	direct method direct method preamalgamation preamalgamation	(3) (*) (2) (*)	16 ± 0.6 (ng/ml) 16.0 (ng/ml) 10.0 (ng/ml) 8.0 (ng/ml)	9.0 (ng/l) 9.0 (ng/l) 9.0 (ng/l)		From the same digest *) Std. addition method *) Std. addition method
C	NBS Oyster Tissue SRM 1566	PTFE bomb HNO_3, 100-110°C 6 hours	direct preamalgamation	(2) (10)	61.5 (ng/g) 61 ± 7 (ng/g)		57 ± 15 (ng/g)	Comment 2) see Fig. 3. Comment 3)
D	Fish homogenate IAEA MA-A-2	PTFE bomb HNO_3, 100-110°C 6 hours	direct preamalgamation	(2) (2)	670 (ng/g) 680 (ng/g)		470 ± 20 (ng/g)	Comment 4) Comment 4)
E	NBS Citrus Leaves SRM 1572	PTFE bomb HNO_3 / $HClO_4$ (4:1), 100-110°C 6 hours	direct preamalgamation	(3) (3)	120 ± 22 (ng/g) 134 ± 15 (ng/g)		80 ± 20 (ng/g)	Comment 4) Comment 4)
F	NBS Coal Fly Ash SRM 1633 a	Erlenmayer flask HNO_3 / HCl 90°C, 90 min	preamalgamation preamalgamation	(4) (3)	254 ± 65 (ng/g) 183 ± 25 (ng/g)		160 ± 10 (ng/g)	Comment 4) Comment 5)
G	NBS River Sediment SRM 1645	Erlenmayer flask HNO_3 / HCl 90-95°C, 90 min	preamalgamation				1.1 ± 0.5 (ug/g)	Comment 6) see Fig. 4.

RESULTS AND DISCUSSION

I) CALIBRATION PROCEDURES

Table 1. shows the instrument responses for mercury standard solutions as obtained using the original procedure. As can be seen, poor reproducibility is obtained below 20 ng Hg. From Table 2., which summarizes results obtained using the modified procedure (reversed addition of reactants), we can see that the reproducibility of the M-511 is better over the whole

Au-film sensor (500 ng Hg). At this point, a 15 min film heating procedure must be activated to desorb mercury from the sensor.

The calibration curve, representing measurement of a 30 ml volume in the JIC reduction vessel, is shown in Fig. 2A.

The sensitivity of the M-511 was observed to be influenced by many unknown factors. Table 3. shows the variation of instrument response for 24 successive measurements of 10 ng Hg within 5 hours under the same experimental conditions.

From Fig. 2 it is clearly seen that sensitivity of the whole procedure for the mercury

determination using M-511 greatly depends on the technique applied. For both methods, aeration-reduction and vapour-injection, greater sensitivity was achieved if a preamalgamation step were used (in Fig. 2, compare 2A with 2C, and 2B with 2D).

II. MEASUREMENT OF SAMPLES

Table 4. shows the results of mercury determinations in various sample matrices using different methods for preparation and measurement. The results obtained are compared to certified values or to values obtained by CVAAS, and commented on below according to the symbols in Table 4.

ad comm. 1.) Good agreement was found between the M-511 and CVAAS methods. As the limit of detection as well as the precision of determination is a function of the mass of mercury (sample size), it can be expected that the M-511 will satisfy requirements for determination of mercury in various types of waters, including coastal sea water, supposing that a sufficient aliquot or/and the double-amalgamation technique were to be applied (HORVAT *et al.*, 1987).

ad comm. 2.) Working with wet digested biological materials, we found serious interferences. Typical behaviour of the M-511 is illustrated in Fig. 3. At point A, 10 ml of reducing medium (1% $SnCl_2$ in 3M H_2SO_4) was transferred to the JIC reduction vessel and then by aeration cycles C its blank value determined (response=0). After calibration of the M-511 with 5 and 10 ng Hg standard solution, 4 ml of sample digest was added to the same reducing medium and two aeration cycles were activated to obtain quantitative recovery of mercury (responses = 6+0). The calibration procedure was repeated with 5, 10 and 20 ng Hg to check the characteristics of the instrument. The contents of the JIC vessel were allowed to stand for 10 minutes and then three aeration cycles were again activated (responses = 10+3+0). At point B new reducing medium was added and the procedure was repeated. Similar results were obtained, as shown in Fig. 3. Correct results could be obtained only if the first response was

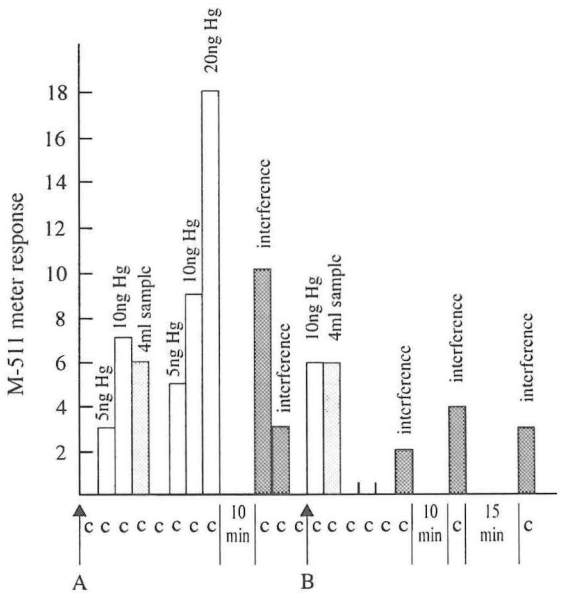

Fig. 3. Measurement of wet digested oyster tissue using the M-511 direct aeration-reduction method.

accepted for calculation, but the phenomenon of interference cannot be ignored.

The measurement of the blank solution (HNO_3 and a mixture of $HNO_3/HClO_4$) resulted in zero response, while measurement of the sample in the presence of $KMnO_4$ (which prevents reduction of Hg ions) resulted in different irreproducible responses. Hence, the observed interferences were probably caused by volatile products which arose from the sample digest during the reduction-aeration cycles. We tried to eliminate acidic fumes from the digest by bubbling them with N_2 for 45 minutes, but interferences were still present.

ad comm. 3.) Using a preamalgamation step (Fig. 1) we obtained good and reproducibile results for the oyster sample. For different amalgamation times (2, 4, 15 min) the same risponse was displayed.

ad comm. 4.) Unfortunately, the preamalgamation step did not result in satisfactory responses for all the samples we tested. The high results obtained for reference materials indicate that positive interferences were still present. As the procedures for preparation of fish homogenate and oyster tissue were identical, the interferences seem to depend on the type of sample matrix.

ad comm. 5.) Using a combination of a preamalgamation step and additional filters (10% NaOH, soda lime - as a trap for volatile substances), an acceptable result was obtained for coal fly ash.

ad comm. 6.) Fig. 4. shows the measurement of river sediment. The method with a preamalgamation step and additional filters (10% NaOH, soda lime) was used. Bubbling of the sample during the reduction - aeration step was performed with nitrogen at a flow rate of 120 l/h, for 2 minutes. A repeated operation cycle on the same sample of standard aliquot always resulted in zero response compared to the first aeration cycle in both cases. However, as is illustrated in Fig. 4., on repeated measurements of fresh aliquots of digest or standard a marked decrease in instrument response was observed. Hence, no analytical result could be obtained.

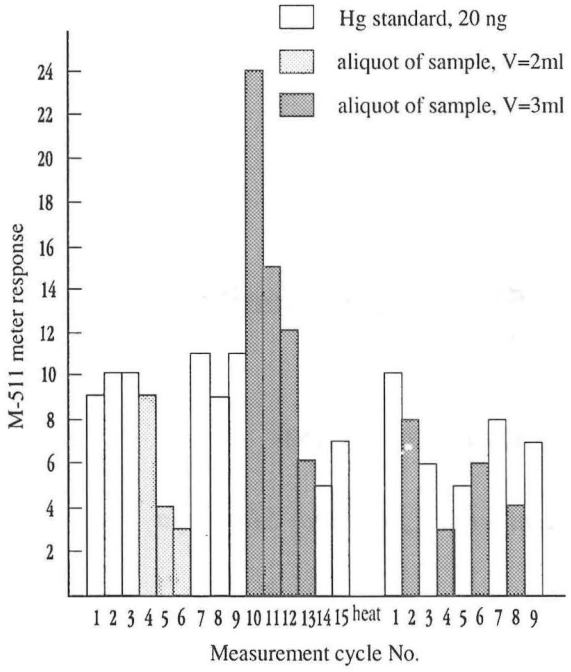

Fig. 4. Measurement of river sediment using the M-511 preamalgamation step and additional filters (10% NaOH, soda lime).

To summarize, serious interferences were found in the analysis of wet digests of real environmental and organic samples. MURPHY (1979) reported that a Jerome Gold Film Mefcury Detector was unaffected by various chemicals dissolved in water. However, no real sample digests were tested in this interference study.

CONCLUSION

The M-511 was calibrated using both reduction - aeration and vapour - injection methods (direct and with preamalgamation step). Good linearity was obtained for both methods in the examined range between 5-40 ng Hg.

Precision is dependent on the mass of mercury in the sample aliquot analysed; when it is above 20 ng Hg, a precision of 6-10% was found.

Day-to-day and within-day variations in sensitivity are inherent to the M-511 and therefore frequent calibration is necessary. The sensitivity of the whole procedure in the mercury determination is greatly dependent on the technique applied.

The efficiency of aeration of mercury from solution is inadequate when working with the orginal JIC reduction vessel; using a modified reduction vessel this can be overcome.

Positive interferences were found when measuring wet digested natural samples. These were probably caused by some volatile substances which are liberated from the digest solution during the reduction - aeration step. The intensivity of the interference was dependent on the type of sample matrix, as well as on the method of preparation of the sample for measurement. In some cases it can be eliminated by using a preamalgamation step, or by introducing an additional filter trap for volatile substances. The sensitivity of the M-511 greatly decreased after measurement of samples which caused interference, probably due to changed characteristics of the Au-sensor.

On the basis of these results and experiments (supposing that the performance of our M-511 is typical), it appears that even if optimal conditions for reliable operation of the instrument could be found such a complex and time - consuming procedure negates the original simplicity of the apparatus. Also, the rather inflexible parameters of the M-511 (flow rate, timing cycle, range of response) are additional

disadvantages compared to a conventional CVAAS system.

ACKNOWLEDGEMENTS

This research was partly financed by the International Atomic Energy Agency, Vienna, under research conctract No 5020/EP.

REFERENCES

DUMAREY, R., E. TEMMERMAN, R. DAMS and J. HOSTE. 1985. The accuracy of the vapour - injection calibration method for the determination of mercury by amalgamation/cold-vapour atomic absorption spectrometry. Anal. Chim. Acta, 107:337-340.

HORVAT, M., T. ZVONARIĆ, P. STEGNAR. 1986. Optimization of a wet digestion method for the determination of mercury in blood by cold vapour atomic absorption spectrometry (CVAAS). Vestn. Slov. Kem. Druš. 33:457-487.

HORVAT, M., T. ZVONARIĆ and P. STEGNAER. 1987. Determination of mercury in seawater by cold-vapour atomic absorption spectrophotometry. Acta. Adriat., 28:59-63.

MCNERNEY, J.J. and P.R. BUSECK. 1972. Mercury detection by means of thin gold films. Science, 178:611-612.

MUDROCH, A. and E. KOKOTICH. 1987. Determination of mercury in lake sediments using a gold film mercury analyzer. Analyst, 112:709-710.

MURPHY, P.J. 1979. Determination of nanogram quantities of mercury in liquid matrices by a gold film mercury detector. Anal. Chem., 51:1599-1600.

SCHROEDER, W.H. and R.A. JACKSON. 1987. Environmental measurements with an atmospheric mercury monitor having speciation capabilities. Chemosphere, 16:183-199.

Accepted: April 2, 1991

Određivanje žive pomoću m-511 živinog monitora s tankim Au-filmom

Mirjana ŠKREBLIN i Anthony R. BYRNE

"J. Stefan" Inštitut, Ljubljanska Univerza Ljubljana, Slovenija

KRATKI SADRŽAJ

U radu je opisano testiranje novog, portabl instrumenta za mjerenje žive, M-511 Gold Film Mercury Analyzer-a (proizvod tvrtke Jerome International Corporation), koji radi na načelu promjene otpora tankog Au-filma kada se ovaj amalgamira u prisustvu elementarnih živinih para.

Za kalibraciju kao i za mjerenje uzoraka, uz originalnu metodu, korištene su i različite modificirane metode radi pronalaženja optimalnih uvjeta mjerenja. Ustanovljeno je da se osjetljivost instrumenta često spontano mijenja tijekom mjerenja, te da osjetljivost cjelokupnog postupka pri određivanju žive znatno ovisi o načinu kojim se živine pare generiraju (redukcija iz otopine ili injektiranje Hg0) i uvode u instrument (direktno ili nakon amalgiranja na Au-absorberu).

Utvrđena je dobra linearnost u ispitivanim granicama od 5 do 40 ng Hg. Preciznost je ovisna o količini žive u mjerenom alikvotu uzorka: za količine veće od 20 ng uobičajena je od 6 do 10%.

Pri mjerenju referentnih tvari različitog matriksa, utvrđene su pozitivne interference (vjerojatno uzrokovane oslobađanjem volatilnih supstanci iz kiselo raščinjenih otopina uzoraka) koje se tek ponegdje mogu ukloniti upotrebom dodatnih filtera i uvođenjem preamalgamiranja - što prvobitno jednostavni postupak pretvara u zamršen.