

Determination of Methylmercury in Sediment Samples by AAS

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In the present study isolation of methylmercury from sediments by steam distillation was investigated. Optimal distillation conditions were found out by distillation of model aqueous samples. The amount of mercury was determined by thermal oxidation-amalgamation technique. Isolation of methylmercury from the samples was approved by an independent method of high-performance liquid chromatography. The recovery of the methylmercury after steam distillation was 97–100 %. The accuracy of the distillation procedure was confirmed by analysis of sediment standard reference material.

It is well known that the toxicity and environmental fate of mercury strongly depends on its chemical forms. Under various natural conditions inorganic mercury may be converted to very toxic monomethylmercury (CH_3Hg^+ abbreviated to methylmercury MeHg) compounds, which tend to bioaccumulate in the aquatic and/or terrestrial food chain. It is estimated that 40–50 % of the Hg^0 cycling through the atmosphere is initially of anthropogenic origin largely due to the combustion of coal, mining and smelting ores (particularly in Cu and Zn smelting), industrial production processes (particularly in the Hg cell chloroalkali process for production of gaseous chlorine and sodium hydroxide) [1].

Although total level of mercury in surface water is very low (20 ng dm^{-3}), bioconcentration factors approach values 10^6 ng dm^{-3} [2]. A large number of waters are affected by widespread air pollution. Very significant in the cycling of mercury is releasing of Hg^0 and other volatile Hg compounds from soils and sediments under natural conditions. Chemical behaviour of mercury in soil has been described by *Steinnes* [1].

The most widespread analytical techniques used for the determination of total Hg in water are cold vapour atomic absorption spectrometry (CV AAS) [3–9] and CV AAS with preconcentration by amalgamation [10–12].

Various other methods for the determination of total mercury have been reported, including atomic fluorescence spectrometry (AFS) [4, 13, 14], flow injection-atomic absorption spectrometry (FI-AAS) [15, 16], and inductively coupled plasma-mass spectrometry (ICP-MS) [17, 18].

However, organomercury(II) compounds such as MeHg are more toxic to human beings than inorganic mercury and therefore speciation of the physicochem-

ical forms in environmental samples is necessary.

A lot of articles for determination of MeHg compounds in biological and sediment samples have been published [4, 19–21]. In general, most of the analytical methods for MeHg are based on the solvent extraction [22, 23], acid leaching [24], alkaline digestion [24], or steam distillation [24–26].

However, the presence of organomercury species in environmental samples at low concentration levels is promoting research of various approaches combining efficient and selective separation techniques with sensitive and selective detection techniques for their analysis. Coupling of liquid and gas chromatography and atomic spectrometry as a detection technique is frequent combination of choice [22, 23, 27–29].

In this contribution a simple technique for isolation of methylmercury from water samples and sediments has been studied. The released methylmercury in distillate and mercury(II) in distillate rest of water samples were determined with TMA-254.

EXPERIMENTAL

Mercury nitrate ($\text{Hg}(\text{NO}_3)_2$, Merck, Darmstadt, Germany) of purity 99 % and methylmercury chloride (CH_3HgCl , Organometallics, USA) of 97–99 % were used. Working standard solutions were prepared freshly every day. All other chemicals as HCl and NaCl were of anal. grade purity.

Four stream sediments (S1, S2, S3, S4) from various positions located in the Ružín dam (Eastern Slovakia) were analyzed. Sediment CRM 580 (Community Bureau of Reference, Brussels) was used as certified reference material (CRM) [21].

Trace mercury analyzer, TMA-254 (Institute of Chemical Technology, Prague, Czech Republic), a

single-purpose instrument, was used for the mercury determination. The working conditions were as follows: radiation source was low-pressure mercury vapour lamp (wavelength 253.6 nm), drying time 60 s, drying temperature 110°C, decomposition time 90 s, decomposition temperature 850°C, carrier gas was oxygen (flow-rate 160 cm³ min⁻¹). Optimum analyzable range was 20 ng of mercury [30].

High-performance liquid chromatograph, LiChrograph (Merck, Darmstadt, Germany) was used throughout the experimental work. For details see Ref. [29].

Cleaning Procedure

Extreme precautions were necessary in order to avoid contamination and/or losses of either inorganic mercury or methylmercury. All chemical glassware was thoroughly cleaned using the following procedure:

New or used glassware was filled with 10 % HNO₃ for 24 h. After being thoroughly rinsed with 1 % HNO₃ and deionized water, it was dried and then kept in a clean place.

Distillation Procedure and Determination of Mercury and Methylmercury

The model water sample (1 µg cm⁻³ of inorganic mercury Hg(II) and 1 µg cm⁻³ of methylmercury), or the sample of stream sediments (2 g), or CRM sediment (1 g) was put into 500 cm³ distillation flask,

and 2 g of NaCl were added. Sample was then acidified with 10 cm³ of 2 mol dm⁻³ HCl. The distillation flask was attached to the splash heads and cooler, and the whole system was left to stand for 1 h. After the heating nests had been turned on, methylmercury was distilled to the receiver containing 2.5 cm³ of the mobile phase for HPLC (acetonitrile : aqueous solution of 1,2-cyclohexylenedinitrilotetraacetic acid (CDTA, $c = 2 \times 10^{-4}$ mol dm⁻³) acidified by H₂SO₄ to pH = 2.0; $\varphi_r = 2 : 8$) [29].

It was necessary to find out optimal temperature for both heating nests. The boiling flask filled with deionized water was heated up to maximal temperature. Other heating nest operated only for tempering of the sample. Under the optimal conditions (temperature, distillation rate) the distillation was completed in approximately 85–90 min.

The distillate and the distillate rest were set to 50 cm³ with deionized water. Distillates should be kept in darkness and cold to avoid decomposition of MeHg by UV oxidation.

The content of methylmercury in distillate and mercury in distillate rest of water samples was determined using a TMA-254 instrument.

RESULTS AND DISCUSSION

Over the first period of our work a distillation apparatus except splash heads was used in order to resolve forms of mercury. Mercury and methylmercury after steam distillation was determined using a single-

Table 1. Contents and Recoveries of Mercury and Methylmercury Determined in Model Samples by TMA-254 after Steam Distillation using Distillation Apparatus a) without and b) with Splash Heads

Sample	Distillate		Distillate rest		
	<i>L</i> _{1,2} /ng	Recovery/%	<i>L</i> _{1,2} /ng	Recovery/%	
1	<i>a</i>	11.46 ± 0.45	57	28.32 ± 0.31	141
	<i>b</i>	19.55 ± 0.16	98	19.98 ± 0.20	100
2	<i>a</i>	12.05 ± 0.18	60	28.42 ± 0.25	142
	<i>b</i>	19.94 ± 0.26	100	20.00 ± 0.36	100
3	<i>a</i>	10.48 ± 0.30	52	29.76 ± 0.30	149
	<i>b</i>	19.64 ± 0.45	98	20.08 ± 0.31	101
4	<i>a</i>	11.26 ± 0.30	56	27.94 ± 0.31	140
	<i>b</i>	20.00 ± 0.41	100	20.04 ± 0.26	100
5	<i>a</i>	11.42 ± 0.35	57	29.04 ± 0.36	145
	<i>b</i>	19.80 ± 0.40	99	19.84 ± 0.31	99
6	<i>a</i>	11.28 ± 0.20	56	29.56 ± 0.38	148
	<i>b</i>	19.54 ± 0.15	98	20.12 ± 0.31	101
7	<i>a</i>	10.66 ± 0.20	53	29.02 ± 0.41	145
	<i>b</i>	19.42 ± 0.30	97	19.63 ± 0.31	98
8	<i>a</i>	11.40 ± 0.26	57	28.82 ± 0.15	144
	<i>b</i>	20.02 ± 0.36	100	19.45 ± 0.31	97
9	<i>a</i>	11.80 ± 0.30	59	28.26 ± 0.26	141
	<i>b</i>	19.80 ± 0.41	99	19.93 ± 0.31	99
10	<i>a</i>	10.52 ± 0.26	53	29.74 ± 0.31	149
	<i>b</i>	19.50 ± 0.26	98	20.05 ± 0.30	100

purpose instrument TMA-254. The amount of mercury introduced into the analyzer was 20 ng. The results are given in Table 1. The recoveries for the methylmercury determined in distillates varied from 52 to 60 %.

The amounts of inorganic mercury determined in distillate rest (recovery 141–149 %) demonstrated that isolation of methylmercury from model samples was not quantitative. The separation of mercury and methylmercury strongly depends on the distillation conditions (distillation rate, temperature) and also on the experience of the personnel performing the distillation.

The time of distillation was 85–90 min using distillation apparatus with splash heads and operating under the optimal distillation conditions. Determined amounts of mercury and methylmercury after steam distillation of model samples using TMA-254 are presented in Table 1.

The confidence intervals $L_{1,2}$ presented in Table 1 were calculated according to [31] from the results obtained on five measurements from water samples after steam distillation. They were calculated at the significance level of $\alpha = 0.05$. The recovery was calculated from the average of five measurements.

The isolation of methylmercury from model water samples by steam distillation was approved by HPLC, as an independent method. The details of chromatographic separation are given in [29]. Chromatogram of separation of mercury and methylmercury after steam distillation in distillate and distillate rest as was detected at 254 nm is shown in Fig. 1.

Isolation of methylmercury from stream sediments was performed using the same procedure as mentioned above. The accuracy of this isolation method was verified by distillation of CRM sediment (certified MeHg value $(75.6 \pm 3.7) \text{ ng g}^{-1}$).

The contents of methylmercury determined by TMA-254 in distillates of samples and CRM after steam distillation are presented in Table 2.

The confidence intervals $L_{1,2}$ for the sediment samples and certified reference material were calculated according to [31] from the results obtained for five measurements. The confidence intervals and the relative standard deviations were calculated on the significance level of $\alpha = 0.05$.

The agreement between the determined content of MeHg in a CRM and the certified value was tested by the Student's and Lord's tests [31]. Both tests proved that there are no significant differences between the certified value of MeHg and the content determined after the distillation procedure.

The detection limit defined as three times the standard deviation of the blank value was 0.25 ng. The blank value is represented by the analysis of blank distillate, e.g. solution of all reagents except the sample (or standard addition of the mercury forms).

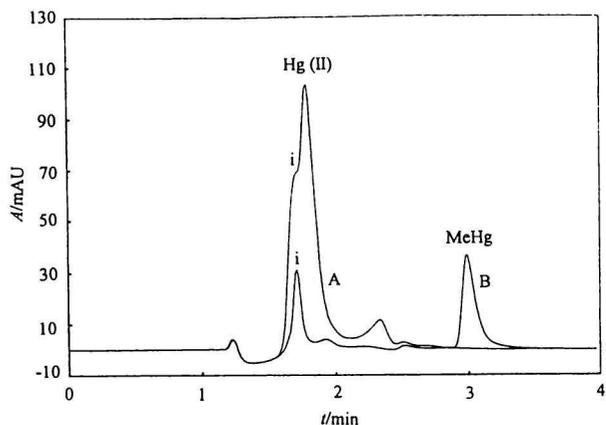


Fig. 1. Chromatographic separation of mercury and methylmercury after steam distillation of their mixture in solution at $1 \mu\text{g cm}^{-3}$ level each by RP-HPLC. A – chromatogram of distillate rest, B – chromatogram of distillate, Hg(II) represents position of mercury elution, MeHg represents position of methylmercury elution, i – unknown impurity, mAU – miliabsorbance unit. Separation conditions: Mobile phase : acetonitrile : aqueous solution of CDTA ($2 \times 10^{-4} \text{ mol dm}^{-3}$) acidified by H_2SO_4 to pH = 2.0; $\varphi_r = 2 : 8$. Column: Separon SGX C 18, particle diameter $5 \mu\text{m}$, CGC 150/3 mm. Flow-rate: $0.5 \text{ cm}^3 \text{ min}^{-1}$. Detection: 254 nm.

Table 2. Determination of Methylmercury Contents in Stream Sediments and Certified Reference Material after Steam Distillation by TMA-254

Sample/CRM	Determined amount $L_{1,2}/(\text{ng g}^{-1})$	$S_r/\%$
S1	150.9 ± 3.0	1.68
S2	66.3 ± 4.0	5.19
S3	55.3 ± 1.5	2.33
S4	118.0 ± 4.7	3.35
CRM 580	71.0 ± 7.5	8.90

Certified value of CRM 580: $(75.6 \pm 3.7) \text{ ng g}^{-1}$.

CONCLUSION

The steam distillation is a suitable method for isolation of methylmercury from various environmental samples. Distillation gives consistent and high recoveries (97–100 %, Table 1) and therefore provides more as low as levels to ppb accurate results especially at low MeHg concentrations.

The amount of sediment taken for direct distillation is basically dependent on the MeHg concentration. It is important to emphasize that with the increased sample mass the limit of quantitation of the method will decrease. This is enabled by the proposed distillation apparatus, till now not used for the purpose.

The second improvement of the proposed apparatus is the use of splash heads, what together with

prolongation of distillation duration increases the efficiency of the procedure up to 97–100 % compared to literature [25].

Detection limit as low as 0.25 ng MeHg was obtained. Analytical quality control (AQC) of the results for MeHg was performed by analysis of CRM certified for MeHg, in contrary to the previous work [24].

This study has shown that distillation is one of very suitable separation techniques for sediment sample pretreatment. Its main advantage is avoidance of matrix interferences which often represent severe limitation of other separation techniques.

The efficiency and selectivity of the isolation of MeHg was approved using independent HPLC method.

Presented results are chosen as representative results obtained during a two-year experience with the procedure.

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