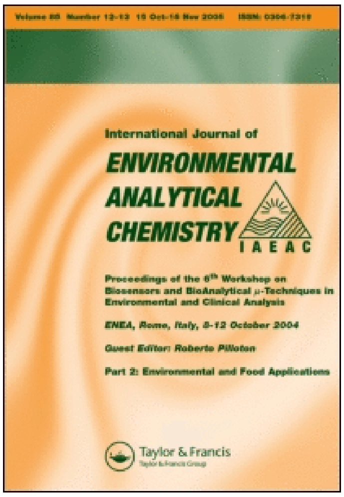

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Preconcentration on Silver Wool of Volatile Organo-Mercury Compounds in Natural Waters and Air and The Determination of Mercury by Flameless Atomic Absorption Spectrometry

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Preconcentration on Silver Wool of Volatile Organo-Mercury Compounds in Natural Waters and Air and The Determination of Mercury by Flameless Atomic Absorption Spectrometry

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Preconcentration of volatile organo-mercury and metallic mercury on silver microcolumn is particularly suitable for the determination in air and water samples. The microcolumn is coupled to a cell for mercury determination by f.a.a.s. With this technique, down to 1 ng of mercury can be determined with a good precision (±15%).

KEY WORDS: Organo-mercury analysis, enrichment of mercury, air and water analysis, flameless atomic absorption of mercury, preconcentration on silver wool.

INTRODUCTION

The most commonly used methods for the determination of trace amounts of mercury in various media are the methods based on flameless atomic absorption spectrometry (FAAS).[1] Since only low concentration of mercury is present in natural waters and in air, the mercury must be preconcentrated. Various preconcentration techniques exist such as in aqueous medium: electrolysis on Au, Pt, Ag, or Cu,[2,3] reduction on copper powder[4] or adsorption on active charcoal;[5] in air: collection on silver wool,[6] on active charcoal[7] or on selective absorption tubes.[8] For the determination of total mercury present, samples of water must be treated with an oxidising agent such as permanganate,[3,9] hydrogen peroxide[10] or ozone.[11]

In our previous work,[11] we had shown that in acidic medium, ionic mercury (labile mercury) directly and the total mercury (except volatile organo-mercury compounds such as dimethyl mercury or diethyl mercury) after having been oxidised with ozone, can be preconcentrated by passing the solution on a microcolumn containing copper powder. Because of the high volatility of dimethyl mercury (DMM) or diethyl mercury (DEM), oxidation by ozone cannot be used for samples containing these compounds.

In this work, we have shown that it is possible to preconcentrate on silver wool microcolumn volatile organo-mercury compounds present in water and in air after carrying out thermal decomposition. Hence contamination of oxidising reagents and loss of mercury are eliminated.

EXPERIMENTAL

Material and reagents

Silver wool, p.a. Merck (because of better amalgamation of gazeous metallic mercury, silver wool is preferable to copper powder). About 0.5 g of silver wool is packed tightly in a pyrex tube (Figure 1e). The silver wool microcolumn is then purified by heating at 400°C under an atmosphere of nitrogen.

Dimethyl mercury solution (Merck, 98%). The concentrated solution is prepared in absolute alcohol and kept at about −18°C in a freezer. Solutions containing 1 to 100 ng/ml were prepared daily in distilled water.

Atomic absorption spectrometer Pye Unicam SP 1900, incorporated with a flameless atomic absorption measuring system is described in our previous work.[11]

SEPARATION FROM WATER

Procedure

The solution (30–500 ml) containing DMM is placed in an aeration vessel (a) (see Figure 1). The system is placed under vacuum and air is bubbled at a fixed flow rate in order to carry off the mercury present already in the metallic form and DMM. The metallic mercury is separated in the first microcolumn containing silver wool placed before the oven (b) and the DMM is decomposed and reduced to metallic mercury in the oven at about 900°C before being separated on the silver wool microcolumn placed after the oven (e). This microcolumn is immersed in a cold bath in order to achieve

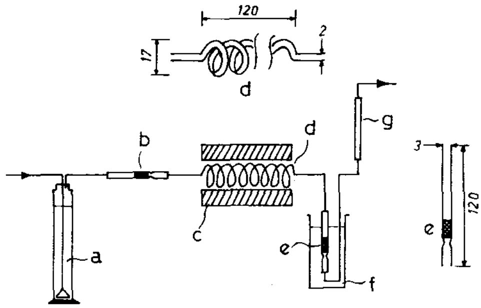

FIGURE 1 System for the separation of volatile organo-mercury compounds in water. (a) Aeration vessel (30–500 ml) with sintered glass (porosity: 2), (b) silver wool microcolumn, (c) tubular oven, (d) spiral of decomposition tube in quartz (number of spiral 17), (e) silver wool microcolumn, (f) cold bath, (g) flowmeter. Dimensions in mm.

quantitative separation of mercury. After the separation, the microcolumn is coupled to a measuring cell for the determination of mercury by FAAS.[11,12]

RESULTS AND DISCUSSION

The first observation that we made was that the rate of bubbling of air has a certain influence on the yield of separation. This is to say that for a given time the volume of carrier gas must be determined in order to obtain a quantitative volatilisation and separation. The yields obtained as a function of rate of flow are given in Figure 2 for a bubbling time of 10 min. By working at a flow rate of 500 ml/min, trial runs have shown that for 2–100 ng of DMM in 500 ml of distilled water, the quantitative separation is reached at the end of 3 min.

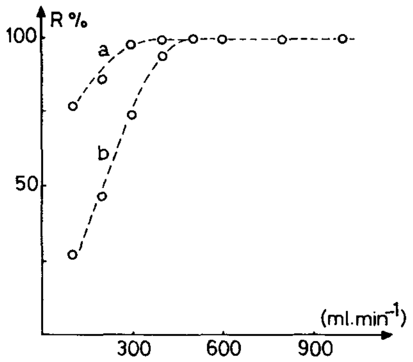

FIGURE 2 Influence of the rate of bubbling on the yield of separation. 44 ng of DMM in 30 ml (a) and in 500 ml (b); bubbling time: 10 min.

However, lengthy bubbling time has no negative effect on the separation.

In order to verify the precision of our technique, we have compared the calibration curve obtained by DMM with that obtained starting from Hg^{2+} solution which has been reduced by $SnCl_2$ using the reduction-aeration technique[13] and separation on silver wool microcolumn under the same conditions, Figure 3. The values of DMM are shown on the straight line in terms of corresponding mercury.

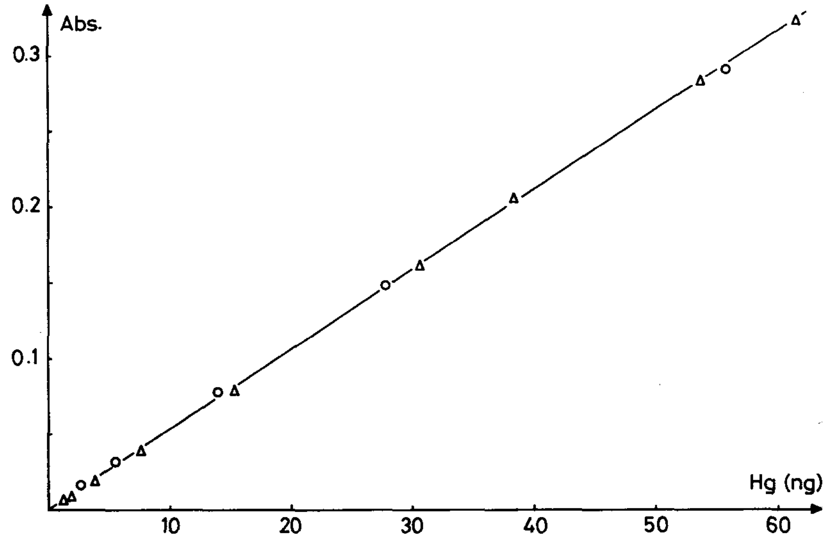

FIGURE 3 Calibration curve, (○) using the reduction-aeration technique and separation on silver wool microcolumn from Hg^{2+} and $SnCl_2$, (△) using the aeration and thermal decomposition technique from DMM. Volume of the solution: 30 ml, bubbling flow rate: 500 ml/min, bubbling time: 10 min.

Separation of metallic mercury and of DMM

By means of our technique, we have shown that a mixture of metallic mercury and DMM can be separated and determined separately. In fact metallic mercury is separated directly on the silver wool microcolumn placed before the oven and DMM is separated after thermal decomposition in the oven on the silver wool microcolumn placed after the oven. The results obtained are given in Table I for both unmixed and mixed metallic mercury and DMM.

We have also checked that the mixture can be preconcentrated on a single silver microcolumn placed after the oven for the determination of total mercury present.

TABLE I

Separation of Hg^0 and of DMM. Volume of the solution: 30 ml, bubbling flow rate: 500 ml/min. (a) Hg^0 prepared from Hg^{2+} and $SnCl_2$ using the reduction-aeration technique. (b) After blank subtraction

		Absorbance obtained (b)	
Hg^0 (a) (ng)	DMM (ng)	abs. due to Hg separated on Ag before the oven	abs. due to Hg separated on Ag after the oven
0	4.4	0	0.021
0	44.0	0	0.205
5.6	0	0.028	0
55.7	0	0.289	0
5.6	4.4	0.030	0.019
55.7	4.4	0.290	0.019
5.6	44.0	0.029	0.196
55.7	44.0	0.284	0.206

Application

For the determination of mercury in water, the sample used directly (without filtering or acidifying) for the separation of volatile organo-mercury compounds. For the determination of ionic mercury and total mercury the method previously described[11] is used. However, the reduction-aeration technique can also be used for the preconcentration on the microcolumn containing silver wool, method similar to that described in literature.[14]

We have analysed a few samples of water from different sources (lake, rivers, tap water). For a volume of 500 ml used for each determination, the concentration of volatile organo-mercury compounds varied between 0–4 ng/l. Furthermore, verification of the precision and reproducibility for the separation and determination was carried out by adding DMM to each sample.

SEPARATION FROM AIR

Procedure and application

For the determination of mercury in air, 15–200 l of air was passed through a silver wool microcolumn at a flow rate of 500 ml/min. Thus the amounts of metallic mercury and organo-mercury compounds on the silver wool placed before and after the oven were determined respectively. Determination of mercury in air was carried out in the research laboratory and in the field. The mercury content depends on parameters such as the temperature, the work load in the laboratories, atmospheric conditions, etc. Some of the results obtained are given in Table II.

TABLE II

Mercury concentration in different samples. (a) An average day of activity in the laboratory, (b) below normal activity, (c) at night, (d) large quantities of metallic mercury used, (e) sunny day

Sample	Date	Volume of air sampled (m^3)	Hg^0 (ng/m^3)	Hg from organo-mercury (ng/m^3)
Atomic absorption lab.	9.9.1977	0.096	66	16 (a)
(continuously ventilated)	12.9.1977	0.096	27	21 (b)
	12.9.1977	0.130	17	8 (c)
Polarographic lab.	13.9.1977	0.048	370	31 (d)
(continuously ventilated)	14.9.1977	0.096	343	34 (d)
Atmospheric air, outdoor	12.9.1977	0.072	21	0 (e)
	13.9.1977	0.192	23	2 (e)

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