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DETERMINATION OF MERCURY IN SEAWATER BY COLD-VAPOUR ATOMIC ABSORPTION SPECTROPHOTOMETRY*

ODREĐIVANJE ŽIVE U MORSKOJ VODI METODOM BEZPLAMENE ATOMSKE APSORPCIJSKE SPEKTROFOTOMETRIJE

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This paper describes a closed aeration technique coupled with a double amalgamation stage on a gold absorber, which is used for the determination of mercury in seawater samples from some different parts of the open and coastal Adriatic Sea.

Mercury analysis was conducted using a LDC-UV monitor (model 1225) equipped with a Hewlett Packard integrator (HP 3390A).

The double-amalgamation stage offers more advantages: the elimination of interferences due to organics or Cl_2 and measurement from the same gold trap which is well characterized. The precision of the method was investigated by determination of total mercury in surface water samples from some different parts of the Adriatic.

The reproducibility was tested by 10 fold measurement of 2 ng Hg^{2+} spikes. The mean value was 1.9 ± 0.4 ng l^{-1}. The detection limit was found to be 0.5 ng l^{-1}.

INTRODUCTION

The mercury concentration of sea water is low and covers the range from 0.5 to 300 ng/l (Friemann and Schmidt, 1982), excluding values from contaminated coastal areas. For the rapid and precise determination of low mercury levels in natural samples the preferred analytical method is cold vapour atomic absorption spectrophotometry. To increase the sensitivity of the method and to separate mercury from interfering substances, a concentration step is needed.

This communication describes in detail a closed aeration technique coupled with a double amalgamation stage on a gold absorber, which is used

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for the determination of total mercury in water samples from some different parts of the open and coastal Adriatic Sea.

MATERIALS AND METHODS

Reagents

$SnCl_2$ (10% in 3M H_2SO_4) was aerated overnight with purified N_2. The $NaBH_4$ solution (1% in 0.05M KOH) was prepared fresh daily and aerated for two hours with purified N_2 before use. Nitric acid was purified by means of a simple »sub-boiling« still, described elsewhere (Tschöpel *et al.*, 1980).

The mercury standard stock solution contained 0.1354 g of $Hg(II)Cl_2$ in 100 ml 1M HNO_3. For the working standard (10 ng $Hg.ml^{-1}$, prepared daily) the solution was diluted with 1M HNO_3.

Cleaning and sampling procedure

The 500 ml pyrex collecting bottles and all other laboratory equipment used for determination of mercury were cleaned firstly by boiling in HNO_3 and secondly in a steaming apparatus for cleaning glassware in nitric acid vapour and then rinsed several times with double-distilled water.

Samples were preserved by immediate addition of 20 ml »sub-boiling« HNO_3 per litre of sea water, which provides a low pH and a strong oxidizing environment required to prevent volatilization losses of mercury. Samples were not filtered to avoid contamination problems.

Procedure

The preacidified unfiltered seawater (500 ml) was digested with 20 ml »sub. boiling« HNO_3 by heating for two hours at 60°C in a stoppered glass flask.

Fig. 1 shows the apparatus used for the reduction-amalgamation step. An aliquot of the digested seawater (50—500 ml) was transferred to a reduction vessel followed by 10 ml of 1% $NaBH_4$ solution. The reduced Hg, purged from the sample for 20 min with precleaned air at a pump flow rate of 30 $l.h^{-1}$, was collected on gold trap connected to the outlet of the reduction vessel. After reduction, the loaded gold trap was disconnected, capped and stored for later or immediate analysis. The gold trap consisted of 0.4g SiO_2 powder (0.3—0.5 mm) coated with gold and contained in a 0.5 cm I. D. quartz tube.

Fig. 2 shows a schematic diagram of the apparatus for determination of Hg from a loaded gold absorber which was connected to a second permanent absorber. The mercury from the first trap was desorbed on to the second permanent gold trap by heating at 650°C for 1 min at a flow rate of 20 $l.h^{-1}$. Then the mercury was desorbed from the permanent gold trap under the same conditions. The mercury released was swept into the optical cell of the LDC-Mercury monitor (Model 1225, $\lambda = 254$ nm). The output signals from this apparatus were fed to an HP-integrator (HP 3390 A) for peak area measurement.

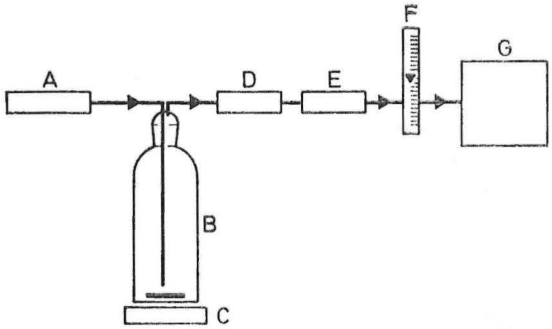

Figure 1. Diagram of reduction amalgamation step

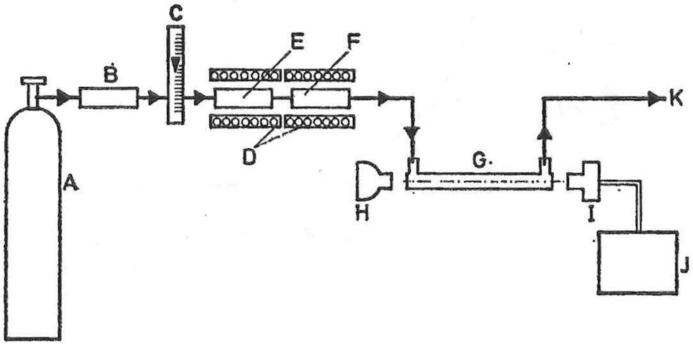

Figure 2. Diagram of apparatus for determination of mercury

RESULTS AND DISCUSSION

Most of the mercury found in surface water is probably in inorganic form as chlorocomplexes. The mercury released after reduction of preacidified water by stannous (II) chloride is conventionally called »reactive« or »easily reducible mercury«. »Total mercury« is that which is released by the same reducing solution after treatment with oxidizing reagents (Bloom and Crecelius, 1983), or UV-radiation (Kiemeneij and Kloosterboer, 1976; Friemann and Schmidt, 1982).

Comparison of tin (II) chloride and sodium borohydride as alternative reducing reagents showed that the calibration graphs were essentially the same and were linear up to 50 ng of mercury with our equipment, and that there were also no differences in the results of total mercury determination. However, the precision of the $NaBH_4$ system was about twice as good as that using $SnCl_2$ reduction.

The aeration time needed for complete reduction of 5 ng of mercury from 500 ml of digested seawater is shown in Fig. 3, which indicates that $NaBH_4$ reduction is more rapid. It can be concluded that the use of $NaBH_4$ is preferable.

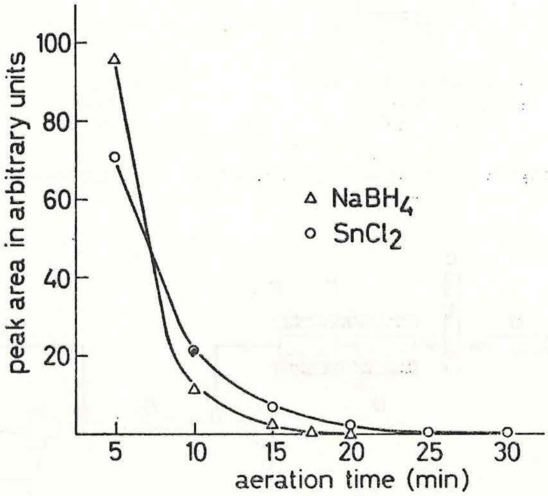

Figure 3. Effect of aeration time on the evolution of mercury vapour (flow-rate of air was kept at 30 l/h)

Table 1. Concentration of total Hg in seawater from different parts of the Adriatic

Sampling area		Total Hg concentration (ng/l)	Number of aliquots	Notes
Open seawater (North Adriatic)	surface	0.9 ± 0.4	8	
	bottom	1.4 ± 0.6	8	
Coastal water (North Adriatic Rovinj)	surface	5.4 ± 2.4	4	
Coastal water (Central Adriatic Kaštela Bay)	surface 200 m from the shore	32.0 ± 3	6	industrial influence
Harbour mouth (Split)	surface	21 ± 2	5	Influenced by municipal sewage effluents
Coastal water (near Split)	surface	15 ± 2	4	Fresh water influence

The double-amalgamation stage offers several advantages: the elimination of interferences due to organics or Cl_2 and measurement from the same gold trap which is well characterized, leading to greater analytical precision.

The precision of the method for real samples was investigated by determination of total mercury in surface waters from some different parts of the Adriatic (Table 1).

The reproducibility was tested by 10 fold measurement of 2 ng.Hg^{2+} or MeHg^{+} spikes. The mean value was 1.9±0.4 ng 1^{-1}. The detection limit was found to be 0.5 ng 1^{-1}.

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KRATKI SADRŽAJ

U radu je opisana tehnika zatvorenog aeriranja sa dvostepenim amalgamiranjem na zlatni absorber, kao jedno od metodoloških poboljšanja za određivanje niskih koncentracija žive u morskoj vodi pomoću bezplamene atomske apsorpcijske spektrofotometrije.

Koncentracije žive u ispitivanim uzorcima mjerene su sa LDC-UV mercury monitorom povezanim na HP 3390 A integrator.

Ustanovljeno je da se primijenjenom tehnikom uspješno eliminiraju nepoželjne interferencije raznih organskih spojeva ili klora, te da su mjerenja sa permanentnim absorberom (definiranih karakteristika) analitički znatno pouzdanija.

Preciznost metode ispitivana je određivanjem ukupne žive u površinskim uzorcima morske vode sa raznih područja Jadranskog mora.

Reprodukcibilnost metode je testirana sukcesivnim mjerenjem dodatka od 2 ng Hg^{2+} (srednja vrijednost je bila 1.9 ± 0.4 ngl^{-1}). Ustanovljena granica detekcije bila je 0.5 ng Hg/1.