Preconcentration of Mercury on Silver Wool and Determination in Natural Waters by Cold Vapor Atomic Absorption Spectrophotometer

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Abstract: The cold-vapor atomic absorption spectrophotometry developed by Hatch and Ott (1) was modified and adapted to our laboratory and used for the analysis of natural water samples.

Since the mercury concentration in natural waters is very low, a preconcentration step is needed. The preconcentration step was achieved by reduction of mercury with $NaBH_4$ or $SnCl_2$ and amalgamation on a silver wool-packed micro-column. The analytical detection of the method which is based on the 3 σ of the blank signal is 0.35 ng/L. The precision (analytical uncertainty) was found to be 12% (RSD).

Different strategies for sampling at depths and at the surface of the sea, various preservation techniques of the water samples, and methods for the decomposition of organic mercury to liberate mercury into solution in inorganic form were also tested.

Key Words: Natural waters, mercury, cold-vapor, amalgamation, silver wool.

Civanın Gümüş Yün Üzerine Ön Derişimi ve Doğal Sularda Soğuk Buhar Atomik Absorpsiyon Spektrofotometrik Tayini

Özet: Hatch ve Ott (1) tarafından geliştirilen soğuk-buhar yöntemi değiştirilerek ve laboratuvarımıza adapte edilerek doğal sularda (deniz, nehir, göl, yağmur suları) civa analizi için kullanılmıştır.

Doğal sulardaki civa derişimi çok küçük olduğu için analiz sırasında bir ön deriştirme yapılması gerekmektedir. Bu çalışmadaki ön derişim işlemi civanın $NaBH_4$ veya $SNCl_2$ ile indirgenip, civanın gümüşle amalgam yapma özelliğinden faydalanılarak içerisine gümüş yün doldurulmuş mikro-kolonda toplanması ile gerçekleştirilmiştir. Kullanılan bu yöntemin gözlenebilirlik limiti (3 σ esas alınarak) 0.35 ng/L olarak hesaplanmıştır. Yöntemin duyarlılığı ise (analitik belirsizlik) (RSD) çalışma süresinde % 12 olarak hesaplanmıştır.

Denizden yapılan örneklemeler için değişik stratejiler ve örneklerin korunması için değişik yöntemler denenmiştir. Organik civanın parçalanarak inorganik hale dönüştürülmesi için ayrıca değişik yöntemler uygulanmıştır.

Anahtar Kelimeler : Doğal sular, civa, soğuk-buhar yöntemi, amalgam, gümüş yün.

S. YEMENİCİOĞLU, I. SALİHOĞLU

Introduction

The mercury concentration of sea water is very low, at nanogram or subnanogram levels excluding the contamined coastal and estuarine waters. The published mercury concentrations in sea water by different authors range from 0.1 ng/L to 50 ng/L (2-15). The most recent findings suggest that open ocean mercury concentrations fall in the range of 0.5-2.0 ng/L (16). In recent years the introduction of precise and sensitive analytical methods has led to an awareness of contamination problems and the care which must be taken to avoid contamination during sampling, storage and analysis. As a result, the more recent data are about one order of magnitude lower then the previous data.

The most widely used analytical method for rapid and precise determination of low mercury levels in natural waters is the cold vapor atomic absorption spectrophotometry developed by Hatch and Ott (1). To increase the sinsitivity of the method and to eliminate interfering substances, a preconcentration step is needed. The reduced mercury can be concentrated in different media. Some authors have used acidic $KMnO_4$ media (enrichment solution) (17-19) and others prefer the amalgamation technique using Cu, Ag and Au (14, 15, 20-22).

The mercury released after reduction by a suitable reducing agent ($SnCl_2$ or $NaBH_4$) from a preacidified sample is conventionally called "reactive" mercury. "Total mercury" is that which is released by the same reducing reagent after treatment of unfiltered sea water samples with chemical oxidizing agents or UV-radiation (photo oxidation).

The detection limit and the precision of the method varies between laboratories and the concentrating media. Analytical uncertainty of 20% RSD has been reported by Horvat et al. (22). Gill and Fitzgerald have reported their analytical uncertainty as 25%, but later they improved their precision of 10% RSD (14). Increased sensitivity can be achieved by using large volumes of sample in the reduction and gas phase collection step.

The amalgamation method of analysis offers several advantages, i.e., the elimination of interferences due to Cl_2 or organics, and analytically defined traps lead to better precision.

Here, we report the method developed and adopted in our laboratory for the analysis of total mercury in natural waters (sea water and river water). Different sampling methods from depths and from the surface water preservation techniques, and decomposition of organic mercury to liberate mercury into solution in inorganic form were also tested to check the contamination problems during sampling, storage, and analysis.

Analytical Procedures

Distilled and deionized water were used to prepare standard and reagent solutions. All solutions were prepared daily and used fresh.

The solutions and samples were prepared in a class-100 clean-air cabinet (Gelaire class 100), maintaining laminar air flow and, thus, positive pressure in the hood.

Standard solution of mercury

The mercury standard stock solution of 1000 ppm was prepared by dissolving 1.35349 g. $HgCl_2$ (Fisher ACS) in 25 ml of concentrated nitric acid and diluted to 1000 mL with distilled-deionized water. The working standards were prepared daily from stock solution by successive dilution.

Potassium permanganate solution

Potassium permanganate solution (5% w/v) was prepared from crystalline $KMnO_4$ (Merck max. 0.000005% Hg, GR, ACS ISO) by dissolving in distilled-deionized water.

Potassium peroxodisulfate solution

Potassium peroxodisulfate 5% (w/v) was prepared by dissolving $K_2S_2O_8$ crystals (Merck GR) in distilled-deionized water.

Hydroxylammonium-chloride

$HONH_3Cl$ 12% (w/v) (Merck max. 0.000001% Hg GR, ACS, ISO) solution was prepared from crystalline hydroxylammonium-choloride in distilled-deionized water.

Tin (II) chloride and sodium borohydride solutions

Tin (II) chloride solution 10% (w/v) was prepared by dissolving $SnCl_2.2H_2O$ (Merck max. 0.000001% Hg GR) in distilled-deionized water. Five mL of concentrated HCl was added to each 100 mL of solution.

$NaBH_4$ solution 2% (w/v) was prepared by dissolving sodium borohydride (Merck GR) in distilled and deionized water and 1 ml of 0.1 N KOH was added to each 100 ml of solution.

Both solutions were purged with mercury free nitrogen gas by stirring with a magnetic stirrer.

Acids and bromine

Nitric acid (Merck 65% max. 0.0000005% Hg GR, ISO) hydrochloric acid (Merck 37% GR max. 0.000005% Hg), sulfuric acid (Merck 95-97% GR, ISO max 0.0000005% Hg) and bromine (Merck 99.5% GR ISO) were used as received.

EPA Samples

The EPA samples were supplied by the U.S. Environmental Protection Agency in ampoules. The concentrates from the ampoules can be diluted to give a range of concentrations.

Preconcentration of Mercury on Silver Wool and Determination in Natural Waters by Cold Vapor
Atomic Absorption Spectrophotometer

S. YEMENICIOĞLU, I. SALIHOĞLU

Microcolumn

The microcolumn used to preconcentrate the mercury was packed with a 0.3 µm diameter silver wire. Prior to use, the column was conditioned at about 500 °C for 24 hours. During the conditioning period, nitrogen gas was allowed to pass through the microcolumn at rate of 100 mL/min.

Instrumentation

The arrangement of the experimental apparatus is shown in Figure 1. The tubing used is made of Tygon (i.d. 0.5 cm) and teflon (PTFE i.d. 0.1 cm). A Varian-Techtron model AA6 atomic absorption spectro-photometer equipped with a Varian hollow-cathode mercury lamp was used for the analysis. The output was routed to a Varian Techtron model 9176 strip chart recorder set on 5 mV to read full scale at 0.5 absorbance unit.
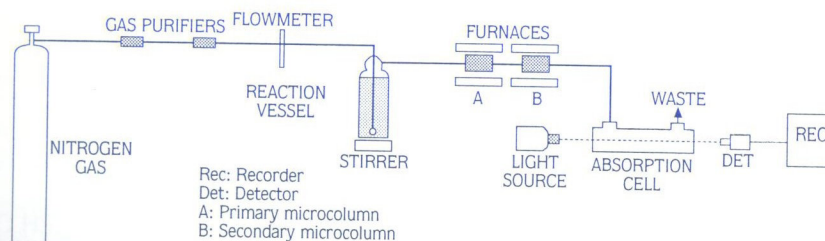

FIGURE 1.   SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS SETUP.

Experimental conditions were adjusted as follows:

Wave length : 253.7 nm

Band width : 0.5 nm

Lamp current : 3 mA

Nitrogen gas flow rate : 600 mL/min.

Cleaning of the Glasswere

The cleaning of glassware is important and needs great care for the reliability and accuracy of the results. During this study the sample containers were cleaned with hot concentrated nitric acid (Merck 65% extra pure). To each bottle, 500 mL of hot acid was added and it was shaken on a shaker for about 2 hrs. and rinsed with distilled-deionized water. The reaction vessels were cleaned by filling them with aqua regia heated to about 70 °C for at least 4 hours, and then rinsed with distilled-deionized water. The reaction vessels were cleaned by filling them with aqua regia, heated to about 70°C for at least 4 hours, and then rinsed with distilled-deionized water. The tubing was washed with 10% hot nitric acid and rinsed with distilled-deionized water.

Sample collection and preservation

Sea water samples were preserved in 1 L capacity amber glass bottles. The bottles were kept in sealed plastic bags before and after sampling. Samples from depths were collected in Nansen bottles or Go-Flo Rosette sampler (General Oceanics Inc.). Surface samples were either collected with a plastic bucked (designed to collect water from about 0.5 m below the surface), or with a plastic centrifuge liquid pump ahead of the bow wake of the ship from 1.5 m below the surface, or directly into the amber glass bottles just below the surface from a rubber boat (about 100 m away from the ship in the direction of undisturbed water). At some stations, multiple sampling was done by different sampling methods to check the effect of various sampling techniques. The sample bottles were then taken into a plexiglass clean cabinet, the preserving chemicals were added, and they were stored at room temperature until analysis. The samples were analyzed within 15-20 days after sampling. During the sampling and storage, great care was taken to avoid contamination.

Preparation of Samples and Analysis

To each sample, 5 mL of concentrated nitric acid and 10 mL of 5% potassium peroxodisulfate were added. Then the samples were heated at 50°C for about 6 hours (this step is necessary for complete decomposition of methyl mercury and phenylmercury). After cooling to room temperature, 12% hydroxyl-ammoniumchloride solution was added until the color of potassium permanganate had disappeared.

For analysis, a 500 mL portion of the water sample was transferred into the reaction vessel, followed by the addition of 10 mL of 2% sodium borohydride solution. The reduced mercury (Hg^0) was purged from the reaction vessel for 30 minutes with mercury free nitrogen at a flow rate of 600 mL/min. and was collected in a silver-packed microcolumn connected to the outlet of the reaction vessel. After the reduction-gas phase collection step had been completed, the loaded microcolumn was coupled with the quartz window absorption cell and mercury was desorbed by heating the microcolumn to about 500°C. The mercury released was swept into the absorption cell for quantitative measurement and the absorption signal was recorded.
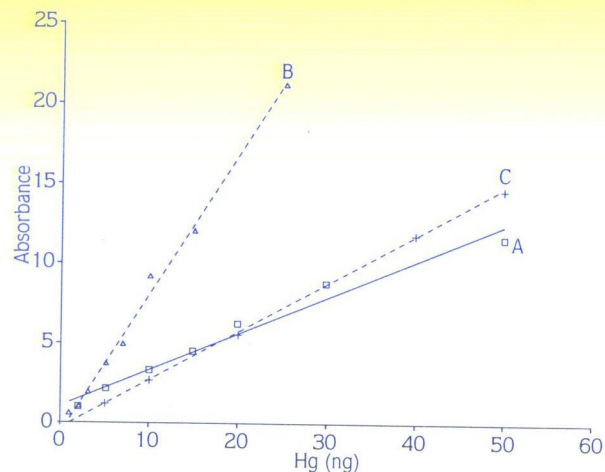
Results and Discussions

Calibration curves

The analytical calculations were done by using calibration curves which were obtained by the standard addition method. The representative examples of the calibration curves ob-

Preconcentration of Mercury on Silver Wool and Determination in Natural Waters by Cold Vapor
Atomic Absorption Spectrophotometer

S. YEMENICIOĞLU, I. SALIHOĞLU

tained during this work are shown in Figure 2. The maximum sensitivity was obtained when NaBH$_4$ was used as the reducing agent and the system was coupled with a silver-packed microcolumn to concentrate the mercury. It was also found that the use of NaBH$_4$ (as reducing reagent) increased the reproducibility.

sampling and analysis are summarized in Table 1. The RSD (relative standard deviation) values are also included for each sampling set of sea water in order to give an idea about the precision of the present work. In Table 5 the precision and the detection limits (although detection limit can be improved by using larger volumes of samples) of several works are given for comparison.

FIGURE 2. CALIBRATION CURVES FOR SEA WATER ANALYSIS. A: WITH SnCl$_2$ AND ENRICHMENT SOLUTION. B: WITH NaBH$_4$ AND SILVER-PACKED MICROCOLUMN. C: WITH SnCL$_2$ AND SILVER-PACKED MICROCOLUMN

FIGURE 3. RECOVERY DEPENDENCY ON FLOW RATE OF CARRIER GAS. A: FOR 10 NG MERCURY. B: FOR 2 NG MERCURY.

The blank checks were done at the beginning of the analysis and repeated after every 10-12 samples were analyzed.

The Recovery Test

The recovery test was done with NaBH$_4$ for 2 ng and 10 ng mercury to optimize the sweep time and nitrogen gas flow rate. The effect of variation of the gas flow rate through sample and the duration of purging time are shown graphically in Figures 3 and 4 respectively. Recovery tests performed by using different gas flow rates indicate that a flow rate between 350 mL/min. and 750 mL/min. is suitable for the mercury analyses under the present experimental setup. The experiments carried out at a flow rate of 600 mL/min gave 87% and 92% recoveries for 30 min and 45 min. of purging time, respectively. The recovery tests were based on EPA standards which contain 0.8 mg of mercury per liter of solution. Since the recovery difference is only 5%, but the latter one needs much more time, a sweep time of 30 min. was preferred at a carrier gas flow rate of 600 mL/min.

FIGURE 4. EFFECT OF STRIPING TIME ON RECOVERY FOR 10 NG HG^{+2}.

Precision of the Method

To check the precision of the method (covering all steps from sampling to the analysis) multiple sea water samples were taken and analyzed. The results obtained for each multiple
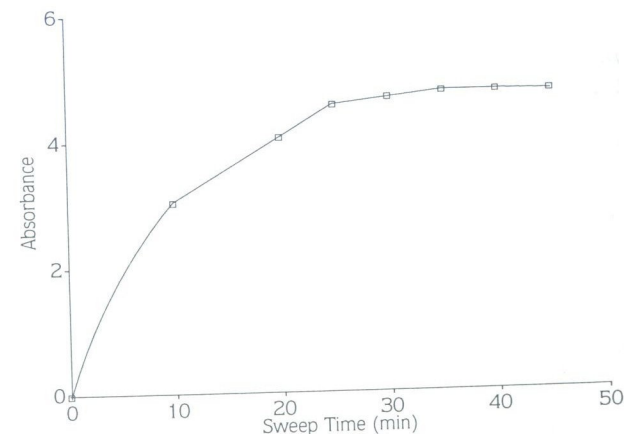
Decomposition of the organic mercury compounds

The decomposition efficiency was tested on samples spiked with CH$_3$HgCl and the results are summarized in Table 2. The tests were carried out using both photo-oxidation (UV-radiation) and chemical decomposition. The test samples were prepared as follows:

Preconcentration of Mercury on Silver Wool and Determination in Natural Waters by Cold Vapor
Atomic Absorption Spectrophotometer

S. YEMENICIOĞLU. I. SALIHOĞLU

TABLE 1.   REPLICATE SAMPLING AND ANALYSIS RESULTS OF SEA WATER SAMPLES

Mercury concentration (ng/L)				
1'st run	2'nd run	3'rd run	Average	RSD %
3.2	3.9	4.5	3.9±0.5	14
4.2	3.2	3.8	3.7±0.4	11
3.6	4.2	3.3	3.7±0.4	10
4.4	3.4	3.7	3.7±0.4	11
3.8	3.1	-	3.4±0.4	10
4.1	5.0	4.3	4.5±0.4	9
3.7	3.2	3.9	3.6±0.3	8
3.2	3.9	-	3.6±0.4	10
3.1	4.3	3.7	3.7±0.5	13
3.5	3.0	4.3	3.6±0.5	15
3.4	4.5	4.4	4.1±0.5	12
3.6	3.0	-	3.3±0.3	9
3.3	3.1	4.2	3.5±0.5	14
4.5	3.6	-	4.1±0.5	11
3.4	3.9	4.5	3.9±0.4	11
4.5	3.6	-	4.1±0.5	11
3.4	4.2	4.3	4.0±0.4	10

TABLE 2.   ORGANIC MERCURY DECOMPOSITION EFFICIENCY OBTAINED BY USING DIFFERENT OXIDATION METHOD.

Method of Digestion	CH_3HgCl standard added ng/L	Hg^{+2} concentration (ng/L)		% reduction of CH_3HgCl
		before CH_3HgCl added	measured after digestion	
10 mL 5% $K_2S_2O_8$ +10 mL HNO_3 Heat 6 hrs 50-60 °C	12.5	2.2	12.0	98
10 mL 5% $K_2S_2O_8$ +10 mL HNO_3 no heating	12.5	2.2	10.5	83
UV-radiation	12.5	2.2	10.0	78
30 min 1 hour	12.5	2.2	11.8	96
20 mL Br_2+10 mL HNO_3 no heating	12.5	2.2	8.2	60
20 mL Br_2+10 mL HNO_3 heat 6 hrs. 50-60 °C	12.5	2.2	8.7	65

The sea water samples were taken into 10 L capacity, acid-cleaned bottle. Before the addition of the organomercury standard, the sea water was stirred with a magnetic stirrer

and sub samples were drawn to estimate the Hg^{+2} content. A mercury concentration of 2.2 ng/L was measured. The sea water samples were then spiked with 250 µL of 0.5 ppm CH_3HCl (12.5 ng/L) which is equivalent to 9.99 ng Hg^{+2}/L of solution, and stirred for 1 hour. To each sample, 10 ml of concentrated H_2SO_4 and 10 mL of 5% $KMnO_4$ was added.

The stock solution prepared in this manner was divided into six subsamples and placed in acid-cleaned bottles. The method of digestion of each set of samples and the quantity of mercury measured after digestion are summarized in Table 2. The photo-oxidation was accomplished by using an immersion type 15 W (Hanau Heraeus) UV light source.

The results of these tests indicate that the digestion was complete when $K_3S_2O_8$ and concentrated HNO_3 were used and this was followed by a heating step. Photo-oxidation by exposing the samples to UV-radiation for 1 hour also resulted in complete decomposition of the organomercurials, and mercury was released into the solution in the form which can be readily reduced by $SnCl_3$ or $NaBH_4$.

Preservation of samples prior to analysis

The water samples used for preservation tests were taken from Lamas Harbour into 20 L capacity-cleaned glass bottle. The sample was spiked with 1.0 mL of 0.1 ppm Hg^{+2} standard. The samples was then irradiated using UV-light source for 1 hour while continuously stirring with a teflon-coated magnetic stirrer. Aliquots drawn from the stock solution prepared in this manner were analyzed to determine the final mercury concentration. The final mercury concentration was found to be 7.9±0.4 ng/L. The stock solution was transferred into acid-cleaned 1 L capacity bottles, similar to those which were used for sea water samples. Twenty bottles of test samples were prepared in this manner. The test bottles were then divided into four groups each of which consisted of five bottles. The results for each set of samples and the preserving method are given in Table 3.

TABLE 3.   RECOVERY OF MERCRY FROM THE SEA WATER SAMPLES PRESERVED WITH DIFFERENT ACIDS AND OXIDIZING REAGENTS

Added*	mercury concentration ng/L			% loss in	
	1st day	after 3 weeks	after 3 months	3 weeks	3 months
5% $KMnO_4$+H_2SO_4	7.9±0.4	7.7	6.8	-	14
5% $KMnO_4$+HNO_3	7.9±0.4	7.3	2.9	8	63
5% K_2Cr_2O7+H_2SO_4	7.9±0.4	7.0	2.0	11	75
5% $K_2Cr_2O_7$+HNO_3	7.9±0.4	6.8	1.5	14	81

*: 10 ml of each chemical was added to the test samples. Concentrated acids were used.

Three weeks later the analyses were repeated on samples from each groups. No measurable changes in the mercury concentration were detected for the samples which were pre-

Preconcentration of Mercury on Silver Wool and Determination in Natural Waters by Cold Vapor
Atomic Absorption Spectrophotometer

S. YEMENİCİOĞLU, İ. SALİHOĞLU

served by the addition of potassium permanganate and sulfuric acid. The mercury loss in the samples which were preserved by addition of nitric acid and potassium permanganate was found to be about 8%. The analysis of samples to which potassium dichromate and nitric acid were added showed 14% loss; while the loss in those samples which were preserved by the addition of potassium dichromate and sulfuric acid was found to be 11%.

Three months of storage of the test samples which had been preserved by the addition of permanganate and sulfuric acid resulted in a 14% decrease in the mercury concentration compared to the initial concentration. The mercury concentration of the other test samples decreased by more than 50% within 3 months (see Table 3).

Sample Collection

Collection of the sample is very important. Especially for volatile compounds like mercury, the contamination hazard is great. Mercury is a very difficult element to measure accurately. Thus, great care must be taken against contamination hazards throughout all steps from sampling to analysis for reliable measurements. The different methods used for sampling show that if care is taken there is no difference between the sampling techniques tested during this study. The results obtained using different sampling techniques are summarized in Table 4.

TABLE 4.   TOTAL MERCURY CONCENTRATIONS MEASURED IN SEA WATER SAMPLES TAKEN BY DIFFERENT TECHNIQUES. SAMPLES WERE COLLECTED DURING THE DIFFERENT CRUISES OF RV/BILIM IN MARMARA SEA DURING 1988 FROM VARIOUS LOCATIONS.

Total mercury (ng/L) in samples collected by

Rubber boat	pump	bucket	sampling date
-	2.8	2.9	February
-	2.7	2.9	
2.8	2.3	-	
3.2	-	3.4	March
2.0	-	1.6	
3.7	-	4.3	July
3.8	4.0	4.0	
4.6	4.4	4.3	
4.3	4.0	4.5	September
3.3	-	2.8	
2.4	-	2.5	
2.8	4.6	3.7	
3.6	-	3.9	
3.6	3.7	3.7	October
2.8	2.3	3.3	
4.1	-	3.7	
3.7	3.4	3.5	December
3.1	-	2.3	
3.0	3.4	3.4	

TABLE 5.   COMPARISON OF THE PRECISIONS AND DETECTION LIMITS OF DIFFERENT WORKERS

Reference no	Author name	Detection limit (ng/L)	Precision %
18	Tuncel et al., 1980[1]	---	10(2)
21	Dogan and Haerdi, 1978	1	15
22	Horvat et al., 1987[3]	0.5	20
23	Millward and Bihan, 1978[1]	---	10(4)
20	Gill and Fitzgerald, 1988	0.84(5)	10
Present work		0.35	12

1: Permanganate +H2SO4 was used as concentreting media. of reduced mercury.

2: covers the reduction-gas phase collection and analysis step

3: Gold was used as concentrating media.

4: determined by standard addition.

5: given in pM unit.

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