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DETERMINATION OF MERCURY IN LAKE
SEDIMENTS BY GOLD FILM
MERCURY ANALYZER

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EXECUTIVE SUMMARY.

The determination of mercury in aquatic sediments is usually carried out during extensive surveys by cold vapor atomic absorption spectrometry. Large laboratories are usually equipped with several atomic absorption spectrometers, one of them designated only for mercury analyses. However, small laboratories have usually one atomic absorption spectrometer which is used for the determination of different elements in a graphite furnace or by flame. Consequently, this spectrometer has to be converted for the determination of mercury to the very specific cold vapor technique. Recently, a reasonably priced gold film analyzer became available for the determination of mercury in water, blood and urine. This analyzer was tested for mercury analyses in lake sediments. A standard sediment was used to determine the precision and accuracy of the method. Results of the determination were compatible with the recommended concentration of mercury in the standard. The investigation was carried out under study no. ECD 236.

MANAGEMENT PERSPECTIVE.

This report provides information on the determination of mercury in lake sediments by a gold film analyzer. This recently available analyzer is reasonably priced and appears to be suitable for determination of mercury in water and lake sediments.

RÉSUMÉ

Le dosage du mercure dans les sédiments aquatiques est habituellement effectué par spectrométrie d'absorption atomique à vapeur froide dans les enquêtes importantes. Les gros laboratoires sont habituellement munis de plusieurs spectromètres d'absorption atomique dont l'un est conçu et utilisé exclusivement pour les dosages de mercure. Toutefois, les petits laboratoires ne disposent habituellement que d'un seul spectromètre d'absorption atomique qui sert au dosage de différents éléments par flamme ou dans un four graphite. Par conséquent, ce spectromètre doit être transformé pour doser le mercure par la technique très spécifique de la vapeur froide. Depuis peu, un analyseur à film d'or servant à doser le mercure dans l'eau, le sang et l'urine est disponible à prix raisonnable. Ce type d'analyseur a fait l'objet d'un essai pour le dosage du mercure dans les sédiments lacustres. Un étalon de sédiments a servi à déterminer la précision et l'exactitude de la méthode. Cet appareil a donné des résultats comparables à la concentration recommandée du mercure dans l'étalon. Ces recherches ont été effectuées dans le cadre de l'étude n° ECD 236.

PERSPECTIVE - GESTION

Le présent rapport porte sur le dosage du mercure dans les sédiments lacustres grâce à un analyseur à film d'or. Cet appareil maintenant sur le marché est offert à prix raisonnable et semble convenir au dosage du mercure dans l'eau et les sédiments lacustres.

DÉTERMINATION DU MERCURE DANS LES SÉDIMENTS LACUSTRES
GRÂCE A UN ANALYSEUR A FILM D'OR

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Un analyseur de mercure à film d'or a été utilisé pour doser le mercure dans les sédiments lacustres. Les étalons de sédiments et de sols ainsi que les échantillons de sédiments ont été extraits à l'aide d'un mélange d'acide nitrique et d'acide chlorhydrique. Des aliquotes d'extraits renfermant entre 30 et 50 mg de mercure ont été dosées par l'analyseur à film d'or. On peut affirmer que l'écart absolu de la méthode étudiée est habituellement de 0,05 ug/g environ et que son exactitude est de $\pm 0,02$ ug/g. Les résultats du dosage du mercure dans l'étalon de sédiments par l'analyseur à film d'or étaient comparables à la valeur recommandée.

Mots clés : Dosage du mercure; sédiments lacustres; analyseur de mercure à film d'or.

DETERMINATION OF MERCURY IN LAKE SEDIMENTS
BY A GOLD FILM MERCURY ANALYZER

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A gold film mercury analyzer was used for the determination of mercury in lake sediments. Sediment and soil standards and sediment samples were extracted by a mixture of nitric and hydrochloric acids. Extract aliquots containing between 30 and 50 ng of mercury were used for the determination by the gold film analyzer. An absolute deviation of approximately 0.05 ug g^{-1} and accuracy $\pm 0.02 \text{ ug g}^{-1}$ can be considered typical for the investigated method. Results of the determination of mercury in the sediment standard by the gold film analyzer were compatible with the recommended value.

Keywords: Mercury determination; lake sediments; gold film mercury analyzer.

INTRODUCTION

The assessment of spatial extent of sediment contamination by mercury often requires analyses of many samples. For example, the concentration of mercury was determined in about 270 and 170 sediment samples during the survey of mercury contamination of Lakes Erie and Ontario, respectively (1, 2). The determination of mercury in sediments during extensive surveys is usually carried out by cold vapor atomic absorption spectrometry. Governmental agencies or other large laboratories are usually equipped with several atomic absorption spectrometers, one of them designated only for mercury analyses. However, small laboratories are often equipped with one atomic absorption spectrometer. Unless the laboratory specializes in mercury determination, this spectrometer is most likely used for the determination of other elements in a graphite furnace or by flame. Consequently, any time when mercury is to be determined in some aqueous or solid samples, the spectrometer has to be converted to the cold vapor technique. Occasionally, the determination of mercury is carried out on a smaller set of sediment samples. For these cases, a reasonably priced, reliable mercury analyzer would be an advantage. Recently, a gold film analyzer became available for the determination of mercury in water, wastewater, urine and blood. The analyzer is based on the proportional increase in resistance of a thin gold film in the presence of mercury vapor and is equipped with a microprocessor

which controls the operation. Mercury vapor reduced from mercury compounds in analyzed solutions is drawn into the analyzer by an internal pump. The gold film sensor adsorbs and integrates the mercury with resulting signal displayed on a liquid crystal display meter. We tested the suitability of the gold film analyzer for the determination of mercury in sediments using certified sediment and soil standards and selected sediment samples from Lake St. Clair, Ontario. This paper describes the procedure and lists the results.

EXPERIMENTAL

Apparatus

The gold film mercury analyzer Model 511 was purchased from Jerome Instrument Corporation, Arizona, USA. The calibration procedure of the instrument was carried out as recommended by the manufacturer.

Reagents

Hydrochloric and nitric acids. Concentrated acids of analytical reagent grade (Merck) were used.

Stannous chloride solution, 10% m/v. Prepared by weighing 3 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, analytical reagent grade, British Drug House) into a 50 ml stoppered bottle. Twenty-eight ml deionized distilled water were added followed by 2 ml of concentrated

hydrochloric acid. This mixture is a suspension and should be stirred continuously during use, and has to be prepared fresh daily.

Deionized distilled water. Distilled water deionized with a mixed bed resin.

Mercury standard solution. A 1000 mg l⁻¹ mercury standard (British Drug House) was used as a stock solution. At the time of analyses of sediment extracts, a calibration curve was prepared using solutions containing 10, 20, 30, 40 and 50 ng of mercury.

Certified sediment and soil standards. The standard sediment WQB-1 (3) was obtained from the Quality Assurance Section, National Water Research Institute, Burlington, Ontario. This standard is a Lake Ontario sediment and has a similar geochemical matrix to sediments of Lake St. Clair. The standard soil S0-2 was obtained from the Office of Certified Reference Materials Project, Canada Centre for Mineral and Energy Technology, Ottawa, Ontario. Analyses of many sediments from Lakes Ontario and Erie revealed a similar geochemical and mineralogical composition as the standard soil S0-2.

Procedure

Lake St. Clair sediments. Surface sediments and sediment cores were obtained at 35 sampling stations at Lake St. Clair, Canada. All sediment cores were divided into 1 cm subsamples. The concentration of mercury was determined in all samples; however, for this report we selected results obtained by analyses of five surface sediment samples randomly chosen from our Lake St. Clair collection. The sediment

samples were freeze dried, sieved through a 841.10^{-6} m size sieve to remove shells and organic debris, and homogenized by grinding to 100.10^{-6} m size using an automatic grinder (Siebtechnik, West Germany). Certified sediment and soil standards were obtained already pulverized and homogenized. Randlesome and Aston (4) tested different digestion procedures followed by cold vapor atomic absorption spectrometry for total mercury determination in sediments, and found that the most efficient rapid extraction was by a mixture of concentrated nitric and hydrochloric acids (9+1). This procedure is similar to that recommended by Jonasson et al. (5) which was used in this work. Standard or sediment samples (0.5 to 1.0 g) were transferred to a clean (washed with 10% m/V nitric acid and rinsed with deionized distilled water), dry 125 ml Erlenmeyer flask. Concentrated nitric acid (20 ml) was added, followed by 1 ml of concentrated hydrochloric acid. The mixture was gently swirled, allowed to stand for ten minutes, and 40 ml of deionized distilled water were added. The flask was placed in a water bath (90°C) and sample digested for 90 minutes with occasional mixing. The flask was then removed from the water bath and allowed to cool to room temperature. The suspension was filtered through a Whatman 40 filter paper into a 100-ml volumetric flask and diluted to the volume with deionized distilled water. A 10-ml aliquot of the extract was pipetted into a 30-ml glass test tube and concentrated nitric acid (2 ml) was added and the content of the test tube was swirled. After five minutes deionized distilled water was added to completely fill the test tube. After ten minutes the solution was transferred to the

reaction vessel of the gold film analyzer and the vessel was attached to the bubbler. Mercury determination was carried out as recommended in the gold film analyzer manual by injection of 1 ml of stannous chloride suspension and switching on the microprocessor. Prior to next analysis, the reaction vessel and the glass bubbler were rinsed several times with deionized distilled water to remove completely any residues of the stannous chloride reactant.

RESULTS AND DISCUSSION

To determine precision and accuracy of the method, mercury was determined in ten individual extracts of the standard sediment WQB-1, seven times in one extract from the standard sediment WQB-1 and in ten individual extracts of the standard soil S0-2.

The concentration of mercury recommended for the sediment standard WQB-1 is $1.09 \pm 0.15 \text{ ug g}^{-1}$ (3). Analyzing ten individual extracts of this standard, we obtained mercury concentration $1.05 \pm 0.11 \text{ ug g}^{-1}$. By seven repetitions of analyses of one extract of sediment standard WQB-1 mercury concentration was $1.11 \pm 0.09 \text{ ug g}^{-1}$. The recommended concentration of mercury in soil standard S0-2 is 0.082 ug.g^{-1} . By analyses of ten individual extracts of this standard, we obtained $0.093 \pm 0.017 \text{ ug g}^{-1}$.

Analytical data as well as means, standard deviations and coefficients of variation from the determination of mercury concentrations in topmost one centimeter sediments from Lake St. Clair are presented in Table 1. These results indicate a better

reproducibility of mercury determination in samples containing concentration greater than 0.10 ug g^{-1} . The concentration of mercury ranged from 8 to 100 ng in 10 ml aliquots of extracts when 1.0 g of sediment was used. The precision and accuracy of the mercury determination by the gold film analyzer depended on the concentration of mercury in extracts. However, an absolute deviation of approximately 0.05 ug g^{-1} and accuracy $\pm 0.02 \text{ ug g}^{-1}$ can be considered fairly typical. An improved precision was obtained when the concentration of mercury in analyzed aliquots ranged between 30 and 50 ng. On the other hand, a greater spread existed at concentrations less than 10 ng which was probably due to the sensitivity of the gold film analyzer meter response at these concentrations. For future analyses, we concluded that repeated determinations are essential for samples outside the range of optimal mercury concentration with following changes: a) use up to 2 g of sediment with expected low concentration of mercury (0.020 ug g^{-1}); b) modify the volume of the sediment extract according to the calculations from the first analysis. There are two important limits which have to be maintained during the analyses: a) the ratio of water to acid has to be always 7.5:1 in the final solution used in the gold film analyzer manufacture to prevent damage to the gold film; b) the final sample volume should not exceed 40 ml to fit into the reaction vessel. The advantage of the gold film mercury analyzer is the selective adsorption of mercury on gold which eliminates any interferences. Murphy (6) tested a gold film mercury detector for the determination of nanogram quantities of mercury in liquid matrices. He added different chemicals to the

analyzed samples and found that no interference existed during the determination of mercury by the gold film detector. However, erroneously high values were obtained using cold vapor atomic absorption spectrometry.

The apparatus requires a small space (about one m² of a laboratory bench) and is portable. Consequently, it is suitable for a field laboratory with available facilities for an acid extraction. Procedures for mercury determination in water, including drinking, surface and saline water as well as municipal and industrial wastes are already described in the analyzer manual. The results of our test indicate that the analyzer is suitable for the determination of mercury in sediments. However, the operation is completely manual. Present price (1986) of the analyzer is about 9,000-\$ (Canadian).

REFERENCES

1. Thomas, R.L.S. and Jaquet, J.-M. 1976. J. Fish. Res. Board Can., 33, 404.
2. Thomas, R.L. 1972. Can. J. Earth Sci., 9, 636.
3. Cheam, V. and Chau, A.S.Y. 1984. Analyst, 109, 775.
4. Randlesome, J.E. and Aston, S.R. 1980. Environ. Sci. Tech. Letters, 1, 3.
5. Jonasson, I.R., Lynch, J.J. and Trip, L.J. 1973. Geol. Survey Can., Paper 73-21.
6. Murphy, P.J. 1979. Anal. Chem., 51, 1599.

**Table 1 Determination of mercury in sediments from Lake St. Clair
($\mu\text{g g}^{-1}$).**

Sediment No. Replicate No.	1	2	3	4	5
1	0.12	0.33	0.38	0.60	0.94
2	0.06	0.23	0.36	0.60	0.90
3	0.11	0.26	0.38	0.56	0.95
4	0.07	0.22	0.45	0.58	0.98
5	0.07	0.24	0.48	0.58	1.01
mean	0.09	0.26	0.41	0.58	0.97
S.D.	0.02	0.04	0.05	0.01	0.04
C.V.%	22.2	15.4	12.2	1.7	4.1