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A Rapid Method Employing Impregnated Charcoal and Atomic Absorption Spectrophotometry for the Determination of Mercury

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A quantitative procedure has been developed for the determination of submicrogram quantities of mercury in atmospheric, biological, and aquatic samples. In the analysis of biological and water samples, organically bound mercury is oxidized with nitric acid, and all mercury present is reduced to the elemental state with stannous chloride. The liberated mercury is driven by an air current through impregnated charcoal for approximately 2 minutes. A glass tube packed with impregnated charcoal is used to take integrated atmospheric samples. All charcoal samples are analyzed directly for mercury with an atomic absorption sampling boat assembly. Measurement of the recorder peak height is used to determine the quantity of mercury present. The total analysis time is less than 5 minutes for aqueous samples, and the minimum detectable quantity of mercury is 0.02 microgram. After collection of mercury, the charcoal samples may be stored for later analysis.

Introduction

UNITED STATES INDUSTRY has used about 75 million kilograms of mercury in this century alone; yet little information is available on the concentration of mercury in industrial plant atmospheres from plant processing or in the aquatic environment after its disposal. Therefore, there is currently widespread interest in the determination of mercury in a variety of materials, so that the full extent of this environmental pollution problem can be evaluated.

Numerous methods[1,2] for the determination of mercury in various samples have appeared in the literature. The colorimetric dithizone method is considered the classical analytical procedure for the determination of trace amounts of mercury in atmospheric,[1] biological,[3] and aquatic[4] samples. However, this method requires considerable skill on the part of the analyst, is not very sensitive, and is subject to a large number of chemical interferences. An extremely sensitive method[5] employing neutron activation analysis has been used to determine mercury in a variety of materials, but this procedure demands the availability of very expensive equipment. More recently, several methods[2,6] involving the use of "cold vapor" atomic absorption spectrophotometry for mercury determinations have been published. The usual atomic absorption technique, which involves aspiration of the sample into an air-acetylene flame, cannot be applied to the determination of mercury unless complicated extraction procedures are first employed. The "cold vapor" methods utilize the high volatility of mercury and its ability to form free mercury atoms without the use of a flame. "Cold vapor" atomic absorption spectrophotometry has been successfully applied to the determination of submicrogram quantities of mercury in samples of water and sediment[6,7] and in such biological materials as urine[8] and tissue.[2] The

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main differences among these methods lie in the procedures used to convert chemically bound mercury to free mercury vapor, which is subsequently determined by its strong light absorption at 2537Å.

Since mercury may be encountered in industry in a variety of forms—as mercury vapor, volatile mercury compounds, or mercury bearing dust—the quantitative determination of mercury in industrial plant atmospheres poses a serious problem to the industrial hygienist. The threshold limit value (TLV) for mercury vapor and for organic mercury compounds (except alkyl) is presently considered to be 0.05 mg/m^3 air.[9] Since repeated time-weighted average exposures to levels of mercury greater than this value may be associated with mercury poisoning, accurate procedures for measuring this concentration of atmospheric mercury in any form are necessary to protect the health of the worker. However, the existing ultraviolet detectors for mercury in air are not very precise, and they are subject to a number of interferences—for example, organic smokes and fumes, and high magnetic fields—which are frequently encountered in the paper and chlorine industries. The use of specially impregnated active carbon as an efficient sorbent for mercury vapor was first proposed by Stock in 1934.[10] In 1957, Sergeant *et al.*[11] at the Ministry of Labor in Great Britain developed a qualitative test for the determination of total atmospheric mercury, based on the retention of mercury vapor on iodized carbon and the collection of mercury-bearing dust with a mineral wool filter. Mercury is volatilized from the active carbon and the filter by ignition, and the resulting mercury vapor reacts with selenium sulfide test paper to give a characteristic stain, which is compared with a set of standards. These workers found that trace amounts of iodine and iron powder greatly increase the absorption efficiency of activated carbon for mercury vapor, without interfering with the recovery of the trapped mercury.

Experimentation recently conducted in our laboratory indicates that the principle of absorption of mercury vapor on activated impregnated charcoal can be applied to the quantitative determination of mercury in a variety of samples. This paper presents procedures employing impregnated charcoal and the atomic absorption-sampling boat system for the determination of submicrogram quantities of mercury in atmospheric, biological, and aquatic samples.

Principle

In the method of Rathje,[8] generally used in this laboratory for the preparation of the standard curve and for the treatment of biological and aquatic samples, the samples and standards are decomposed with concentrated nitric acid, and the mercury ions in solution are reduced to the elemental state with stannous chloride. In the analysis of tissue samples, crysteine hydrochloride is also added in order to break down all organic mercury complexes present.[2] The mercury is then released from solution by bubbling air through the apparatus. We have modified this procedure, so that the air is then passed through a tube of impregnated charcoal.

Equipment and Reagents

Experimental Apparatus

The relatively simple test apparatus is shown schematically in Figure 1. It consists of a tank of compressed air, a metal needle valve to control airflow, a rotameter covering a range of 0 to 5 liters/min, a 100-ml glass bubbler flask, a 25-ml burette,

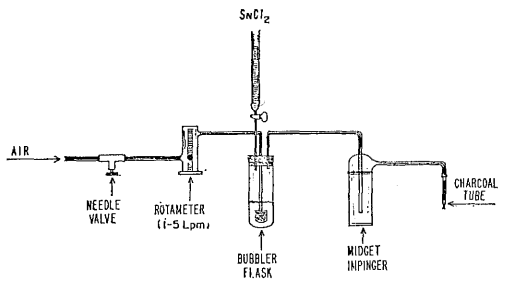


FIGURE 1. Schematic diagram of test apparatus.

and an all-glass midget impinger to act as a safety trap in case of overflow from the bubbler flask. At the end of the system is a straight glass tube (2 inches long) containing approximately 180 mg of 20/40-mesh activated impregnated charcoal (Barnebey-Cheney Co.,* Columbus, Ohio, Type 580-13 or 580-22). The charcoal in the tube is retained by a glass wool plug at the tapered outlet end. All components of this system are connected by minimum lengths of glass and Tygon tubing. *It should be noted that in all the procedures to be described in this paper the present commercially available impregnated charcoal must be heated in a muffle furnace at 600° to 800°C for one hour, prior to use.* This procedure removes excess impregnant and all interfering volatile organic solvents from the charcoal.

A Perkin-Elmer Model 403 atomic absorption spectrophotometer, equipped with a Model 165 recorder, a single- or triple-slot burner head, a sampling boat system, and an Intensitron mercury hollow cathode lamp, was used for all mercury determinations. The mercury resonance line at 2537Å and analytical conditions as recommended by the instrument manufacturer[12] were used. The concentration control was set to about 150, corresponding to a scale expansion of about 5×. The recorder was set to 0.25 absorbance unit full scale, and a chart speed of 20 mm/min.

Reagents

Stannous chloride solution, 20% in 6*N* HCl

Concentrated nitric acid

Antifoaming Solution, 5%: Suspend 5 ml of Dow Corning 702 fluid in 95 ml of water.

Cysteine hydrochloride solution, 1% in 2*N* HCL

Standard Solutions

A 1-mg/ml solution was prepared by dissolving 0.1 gm of metallic mercury in 5 ml of concentrated nitric acid, and diluting to 100 ml with distilled water. A standard stock mercury solution of 100 μg/ml was prepared by pipetting 10 ml of the 1-mg/ml solution into a 100-ml volumetric flask and diluting to volume. This solution is stable for at least four months.

A standard working solution, containing 1 μg of mercury per milliliter, is prepared daily by pipetting 1.0 ml of the standard stock solution into a 100-ml volumetric flask. Two milliliters of concentrated nitric acid is added, and the solution is brought to volume by diluting with distilled water. This working solution should be prepared immediately before use.

Preparation of the Standard Curve

A measured quantity (0 to 1 ml) of the working standard solution is pipetted into the 100-ml bubbler flask. Five milliliters of concentrated nitric acid is added, and the volume is brought up to 50.0 ml by diluting with distilled water (approximately 25°C). One milliliter of stannous chloride solution and one drop of antifoaming solution are added. The flask is swirled gently and connected to the bubbler tube, and air is generated through the system at a rate of 2 liters/min for 2 minutes. (The air pressure should be so adjusted that merely opening the needle valve gives the desired flow rate.) The charcoal tube is removed, and the charcoal introduced into a small boat-shaped tantalum vessel, which is inserted directly into an oxidizing air–acetylene flame. The sampling boat system is shown in Figure 2. Recorded peak height is proportional to the mercury content of the standard. Appropriate quantities of the standard working mercury solution are used to provide a convenient curve for the particular samples to be analyzed. A series of typical recorder tracings for various amounts of mercury is shown in Figure 3. Note that moving the sample boat into the flame removes part of the flame from the hollow cathode beam, producing a negative absorption. This lower absorption level is taken as the base line. The standard curve of micrograms of mercury versus recorder peak height is prepared daily and is used for atmospheric, biological, and aquatic samples.

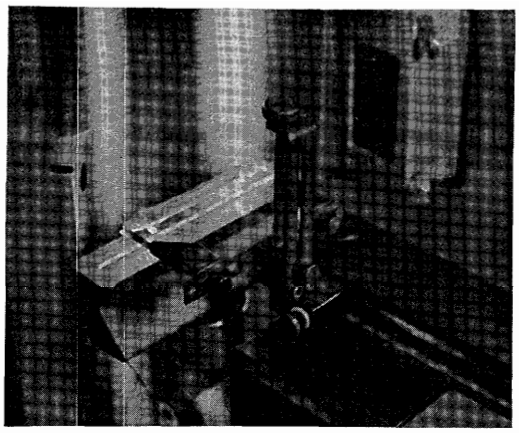
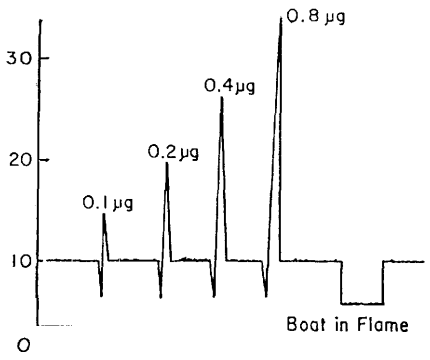


FIGURE 2. Photograph of sampling boat system.

Experimental Procedure

Mercury in Air

Straight glass tubes (6 inches long, 4 mm in diameter), packed with two 1-inch sections (180 mg each) of 20/40-mesh activated impregnated charcoal, are used to take industrial atmospheric samples. The two charcoal sections are separated and retained by fiberglass plugs. An example of the charcoal sampling tube used in this study is shown in in Figure 4. A smaller sampling tube recently developed in this laboratory, is also shown. This tube consists of an inlet section of 100 mg. of charcoal and an outlet section of 50 mg. of charcoal.



MERCURY ON CHARCOAL WITH SAMPLING BOAT

FIGURE 3. Typical recorder tracings for various amounts of mercury.

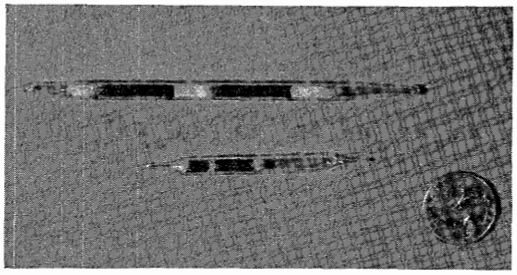


FIGURE 4. Examples of atmospheric charcoal sampling tubes used in this study.

Immediately prior to use, the flame-sealed ends of the tube are broken and an integrated air sample is taken, using a small portable pump to draw a measured amount of air through the charcoal tube. The tubes are sealed with masking tape immediately after sampling and are transferred to the laboratory for analysis. The sealed tubes may be stored in the laboratory at room temperature as long as one month before analysis. The tubes are carefully broken at the time of analysis to remove the charcoal and the glass wool.

A typical charcoal sampling tube for atmospheric mercury is shown schematically in Figure 5. Each charcoal section is analyzed separately; the one nearest the pump is designated section C, while the other is marked section B. The glass wool plug, A, at the inlet end of the tube, is also analyzed for total particulate-bound mercury. The charcoal is removed from the tube, and analyzed by atomic absorption spectrophotometry, using the sampling boat system, as previously described. The mercury content of the sample is read directly from a previously prepared standard curve. Charcoal section B has been found to trap all mercury vapor in the air sample; charcoal section

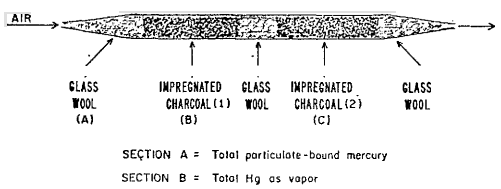


FIGURE 5. Schematic diagram of charcoal sampling tube.

C may be considered a blank, since it has never been found to contain mercury under normal sampling conditions.

Mercury in Urine

Two milliliters of the urine specimen is transferred to the glass bubbler flask, and the sample is then treated exactly as the standards.

Mercury in Tissue

Mercury in biological tissue was analyzed by first homogenizing the tissue with a Teflon homogenizer. Depending on the weight of tissue, a 30-mg/ml or 50-mg/ml homogenate was prepared by diluting with distilled water. A measured aliquot of the homogenate was introduced into the bubbler flask, and 20 ml of cysteine hydrochloride solution was added. The sample is then treated in the manner previously described for standards and urine samples.

Mercury in Water

Water samples are routinely analyzed by transferring a 50-ml aliquot into the bubbler flask, adding cysteine hydrochloride reagent as for tissue, and then treating the sample in the manner previously described for standards and urine.

Results and Discussion

In the determination of atmospheric mercury with the present procedure, one is able to analyze separately for volatile mercury metal and mercury compounds, as well as for mercury-bearing dust in the plant atmosphere. The total analysis time for one air sample is less than 3 minutes.

The limits of detection of the present method for atmospheric samples are shown in Table I. It can be seen that, for a 10-liter (0.01-m^3) air sample, as little as 4% of the TLV for mercury vapor and for inorganic and organic mercury compounds can be detected, or as little as 20% of the TLV for alkyl mercury. The existing ultraviolet spectrophotometric methods have been unable to determine atmospheric mercury vapor precisely at levels less than 40% of the TLV in a 1.0-m^3 air sample. This might explain the previous lack of correlation between atmospheric mercury and biological indices of mercury exposure.

TABLE I
Determination of Mercury in Atmospheric Samples

Type of Exposure	TLV (mg/m^3)	Detection Limit (10-liter air sample)	
		μg Hg	% TLV
Mercury vapor, inorganic and organic mercury compounds (except alkyl)	0.050	0.02	4
Alkyl mercury	0.010	0.02	20

In the analysis of air samples, no significant difference in mercury content was found between samples analyzed directly by the boat without prior desorption of mercury, and identical samples analyzed by first desorbing mercury from the charcoal and glass wool plug by the method decribed for standards and urine samples. Thus, the former procedure was chosen for atmospheric mercury analyses, because of its advantages of simplicity and time over the desorption method.

It is well known that certain organic solvents—benzene, toluene, acetone, and carbon tetrachloride—which absorb 2537 Å radiation, are often present in the industrial atmosphere. However, we have found that levels much greater than the threshold limit values of these solvents must be present before sufficient amounts are adsorbed on the charcoal to interfere with the analysis of atmospheric mercury.

Urinary mercury is frequently used in industrial hygiene as a field control to determine whether a worker has been recently exposed to mercury vapor. The normal level of mercury in urine is considered to be zero; however, this level may rise to 0.020 mg/liter in persons with amalgam dental fillings. A hazardous exposure is believed to exist when the urinary excretion of mercury rises to 0.250 mg/liter.[13] With the Perkin-Elmer 403 used in our laboratory, as little as 0.004 mg of mercury per liter of urine can be detected, using a 2-ml sample. By simultaneously treating a series of urine samples, as many as twenty analyses can be performed in an hour.

Two studies were conducted to evaluate the present procedure for urinary mercury. In the first study, the percentage recovery of known amounts of mercury from previously analyzed urine specimens was determined. Various volumes of the working standard solution were added to 2-ml aliquots of previously analyzed urine, and the sample was carried through the entire procedure previously described. The results of this study are shown in Table II.

In the second study, the results obtained by the present method were compared to the results obtained on the same series of specimens by the method of Hatch and Ott[6]—an extremely sensitive "cold vapor" atomic absorption procedure. The data obtained in this comparison are shown in Table III. It can be seen that the results of the two techniques agreed very favorably.

The comparative results of tissue mercury analyses by the present method and by the method of Hatch and Ott[6] are shown in Table IV. The two techniques agreed favorably in cases where sufficient mercury was present in the tissue for analysis. The data presented here are in agreement with the data of others[14] who have found that the kidney is the concentrator organ for inorganic mercury, with lower concentrations in the liver and brain.

TABLE II
Recovery of Mercury from Urine

Mercury Added (μg)	Mercury Found (μg)	Recovery (%)
0.100	0.100	100
0.200	0.190	95
0.500	0.474	96
0.700	0.670	96
1.000	1.020	102

TABLE III
Comparative Results of Urinary Mercury Analyses of Exposed Workers by Two Methods

Sample No.	Mercury Concentration (mg/liter)	
	Present Method (1)	Hatch/Ott (2)
1	0.015	0.015
2	0.094	0.100
3	0.110	0.115
4	0.160	0.155
5	0.360	0.350
6	0.525	0.550
7	0.732	0.750
8	1.520	1.550
	$r_{1,2}=0.99$	$P<0.01$

TABLE IV
Comparative Results of Mercury Analyses in Tissue Samples by Two Methods

Animal	Dose (mg Hg/kg)	Tissue	Hg (μg/gm tissue)	
			Present Method	Hatch/Ott
Guinea pig	1.0	Kidney	22.2	19.3
		Liver	0.3	0.4
Rat	0.1	Spleen	<0.3	<0.2
		Kidney	0.3	0.2
		Liver	<0.1	<0.1
		Brain	<0.1	<0.1

The comparative results of the present method and the method of Hatch and Ott[6] for a series of 50-ml water samples is shown in Table V. The present method has not been found to be as sensitive as the "cold vapor" atomic absorption procedure for levels of mercury in water less than 2.0 μg/liter and for mercury in river sediments. For values greater than 2.0 μg/liter, the agreement between the two methods has been good. This difference might be explained by the more efficient sample digestion procedure used in the method of Hatch and Ott.[6]

The sensitivity of the present methods for tissue and water samples might be enhanced if more efficient sample preparation procedures were employed. A brief study is now being made to investigate this possibility.

The meter reading of a mercury vapor detector at the outlet end of the test system was used to determine the time required to evolve all mercury from a liquid sample in the round bottom flask. It was found that the evolution of mercury from the sample is completed in less than 2 minutes when an airflow rate of 2 liters/min is employed.

TABLE V
Comparative Results of Mercury Analyses in Water Samples by Two Methods

Sample	Hg (50-ml sample) (ppb)	
	Present Method	Hatch/Ott
A	N.D.[a]	0.3
B	4.0	4.2
C	5.9	6.3
D	3.4	4.2
E	155.0	170.0

[a]N.D. = not detected.

Since the determination of mercury by the procedures described does not involve the introduction of a liquid solution into the tantalum sampling boat, the drying period usually associated with sampling boat analyses is not encountered here. This leads to considerable improvements in reproducibility and sensitivity over previous sampling boat techniques. To avoid excess handling of the boats by the analyst, the charcoal is removed from the boat by vacuum suction after each mercury determination. The effect of the age of the boat on the sensitivity of the analysis has been discussed by Kahn and Sebestyen.[15] A standard should be repeated after every four or five samples to determine if the sensitivity has changed significantly during the course of the analysis. The boat is discarded, and a new one is substituted, when the analytical sensitivity falls to about 75% of the initial value.

Summary

A rapid method employing impregnated charcoal and atomic absorption spectrophotometry has been described for the determination of submicrogram quantities of mercury in atmospheric, biological, and aquatic samples. The total analysis time is less than 3 minutes for atmospheric, urine, and aqueous samples, and less than 5 minutes for tissue samples. The minimum detectable quantity of mercury is 0.02 μg. No prior digestion of biological samples is necessary.

It is hoped that this simple and accurate technique for determining mercury in atmospheric and urine samples will aid future work in occupational health by clarifying the correlation between the amount of mercury excreted in the urine and the amount present in the work environment, and thereby helping to provide an optimum atmospheric environment for the worker.

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