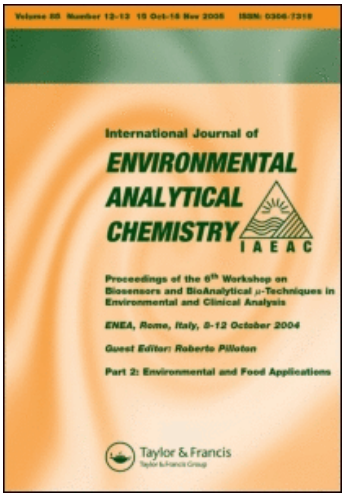

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Determination of Trace Levels of Mercury in Effluents and Wastewaters

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Concern about mercury pollution of the environment and the inapplicability of natural water methods necessitated development of a procedure for determining parts per billion mercury in effluents and wastewaters containing large amounts of organic matter. The sample is digested with sulfuric and nitric acids to destroy the organic matter, and the ionic mercury is reduced to the elemental state by stannous ion. Then the digestate is aerated with a stream of air to carry the mercury vapor through a heated line into a quartz cell positioned in an atomic absorption spectrophotometer for measurement. Analyses of effluents and aqueous samples gave good recoveries of added mercury. Effluents, wastewaters, water supplies,and aqueous samples secured within manufacturing plants have been analyzed. With minor modification, the procedure has been applied to manufacturing materials such as vinylpyridine, latex, sizing, dyes, caustic, and hydro.

INTRODUCTION

The concern about mercury pollution in the environment, particularly in natural waters, has led to the development of analytical procedures suitable for determining this element in natural waters.[1–5] At the same time, this increasing concern has emphasized the need for rapid analytical capabilities to measure mercury at the parts-per-billion level in effluents discharged to the environment. Examination of the literature shows that, contrary to expectations, there appears to be little information available on determining mercury in wastewaters and effluents.

Most natural waters generally contain a relatively small amount of organic matter[6] which is easily destroyed through mild chemical oxidation. When determining mercury in natural waters, the water is acidified and then treated with potassium permanganate and potassium persulfate to destroy organic matter. After reduction to the elemental state, the resulting metallic mercury is usually collected by aeration for measurement, but in some procedures amalgamation and other techniques[1,2,7] are used to isolate the mercury. In the final step of the various procedures, the mercury vapor is measured by flameless atomic absorption.

In contrast to natural waters, many effluents from manufacturing processes often contain a variety of organic compounds[8] in amounts sufficient to interfere in many types of analyses. When the mercury methods for natural waters were applied to effluents from different sources, the results were not satisfactory. During the aeration of many treated effluents, copious amounts of foam filled the aeration apparatus and prevented measurement of the elemental mercury. Although addition of antifoam agents tended to suppress formation of foam, the agents had an adverse effect on the analytical data. Apparently the permanganate-persulfate reagent used in these methods does not completely destroy some types of organic matter present in effluents. Treatment of these effluents with other oxidants under similar conditions did not completely destroy all organic matter in many cases.

Because the existing methods proved unsuitable for effluents, a wet digestion procedure was developed to remove all organics and to eliminate the foaming problems. In this procedure, the sample is chemically treated to remove organic matter, decompose organomercurial compounds, and solubilize inorganic mercury compounds. The ionic mercury is then reduced to the elemental state by addition of stannous ion. Then the mercury vapour is carried by a stream of air or inert gas through a heated line into a quartz cell positioned in the light path of an atomic absorption spectrophotometer. The absorption of radiation at 253.7 nm, a function of the quantity of mercury present, is measured and recorded on a chart. The sensitivity and reproducibility of the method were increased by using a heated glass line rather than a desiccant in the aeration apparatus.

EXPERIMENTAL

Apparatus

Atomic absorption spectrophotometer A Perkin-Elmer 303 atomic absorption spectrophotometer equipped with a recorder readout, a Perkin-Elmer 196 recorder, and a mercury hollow-cathode lamp were used. The burner head was replaced with a custom-made cell holder.

Aeration apparatus The aeration apparatus, shown schematically in Figure 1, consisted of a cylinder of compressed air, a flowmeter, a three-way Teflon stopcock, a 250-ml gas washing bottle, a 10-cm quartz cell (Hellma No. 120-QS) with two filling tubes, and glass lines. The gas washing bottle, equipped with a medium-porosity fritted bubbler, had a 100-ml mark scribed on the outside. The quartz cell and the glass line from the gas washing bottle

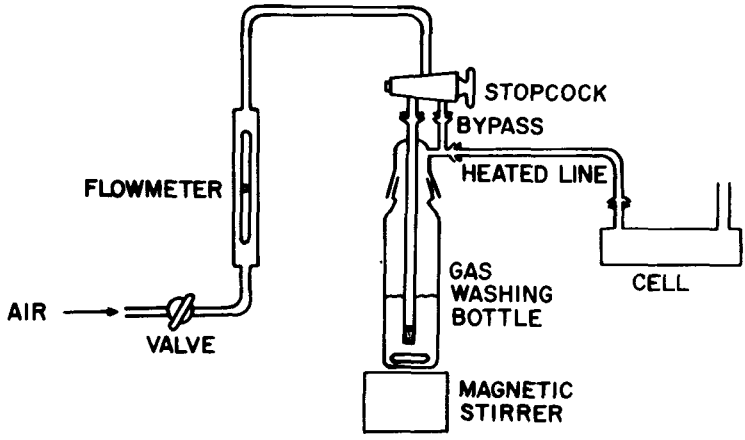

FIGURE 1 Aeration apparatus.

to the cell were heated by an electric heating tape. Viton O-ring ball and socket joints (Berkeley Glasslab Nos. BG 9017 and BG 9018) connected the stopcock to the heated line and the gas washing bottle. Teflon-coated ball and socket joints (Berkeley Glasslab Nos. BG 9028 and BG 9029) connected the heated line to the gas washing bottle and the quartz cell.

Reagents

Reagent-grade chemicals and distilled water were used for preparation of all solutions.

Sulfuric acid, 1 N Add 83 ml of concentrated sulfuric acid to 3 l of distilled water in a glass bottle.

Sulfuric acid, 1 : 3 Add slowly, with stirring, 100 ml of concentrated sulfuric acid to 300 ml of distilled water. Cool and store in a glass bottle.

Stannous chloride solution Dissolve 10 g of stannous chloride dihydrate in 85 ml of distilled water acidified with 15 ml of concentrated sulfuric acid.

Stock mercury solution Dissolve 0.1000 g of redistilled mercury in a minimum amount of nitric acid. Transfer to a 1-liter volumetric flask and dilute to volume with 1 N sulfuric acid.

Standard mercury solution A Pipet accurately 10 ml of the stock mercury solution into a 100-ml volumetric flask. Dilute to volume with 1 N sulfuric acid.

Standard mercury solution B Pipet accurately 10 ml of standard mercury solution A into a 1-liter volumetric flask and dilute to volume with 1 N sulfuric acid.

Instrument settings

The spectrophotometer and recorder readout settings were as follows: wavelength, 253.7 nm; slit, 4; gain, 4 or as required; lamp current, 10 mA; scale expansion, 3X and 10X for low and 1X for high mercury concentrations; noise suppression, 2. The recorder range was 10 mV and the chart speed was 20 mm/min. The air flow was maintained at 1 l/min.

Calibration

For low mercury concentrations requiring analysis at a scale expansion of 3X or 10X, prepare calibration solutions by pipetting 2, 5, 7, 10, 20, 30, and 50 ml of standard mercury solution B into 1-liter volumetric flasks. Dilute each to volume with 1 N sulfuric acid. For the higher concentrations of mercury measured at a 1X setting, dilute 20, 40, 70, 100, and 130 ml aliquots of standard mercury solution B to 1 l with 1 N sulfuric acid.

Pipet 100 ml of a calibration solution into the gas washing bottle which contains the stirring bar. Inject 2 ml of the stannous chloride solution into the bottle and aerate as described in the section under "Procedure". Repeat twice for each calibration solution. Average the measured peak heights from three analyses of each calibration solution, and, if necessary, correct for the blank obtained with 1 N sulfuric acid. Plot calibration graphs of peak height versus mercury content in micrograms.

Procedure

Glassware preparation Clean all glassware, cell, and glass lines with a dichromate-sulfuric acid solution, rinse thoroughly with distilled water, and dry in an oven at 105°C.

Sampling Collect samples in jars, cleaned in the above manner, by rinsing the jar at least twice with the sample before filling and sealing.

Digestion To digest an effluent, shake the sample jar to thoroughly mix the sample and to determine if the sample foams. Then weigh duplicate 100-ml portions of the effluent into 125-ml Erlenmeyer flasks. Add 6 ml of concentrated sulfuric acid, 3 ml of concentrated nitric acid, and several porous silica boiling stones (Cargille) to each flask. If the sample foams when shaken, add three drops of Dow Corning Antifoam H-10 Emulsion (diluted 1: 9) to each flask. Hang a glass hook on each flask lip, and place a small, short-stem funnel in each flask opening.

Place the flasks on a hot plate which is at a temperature of about 200°C. The flask contents will begin to boil smoothly in a few minutes without bumping or loss. Continue boiling until the sample is reduced to sulfuric acid fumes. When the digestate begins to darken, slowly flow down the flask walls from a dropper enough concentrated nitric acid to clarify the solution. Allow the nitrogen oxides to dissipate from the flask. Repeat this addition of concentrated nitric acid as needed until the digestate remains clear. Then flow two additional $\frac{1}{2}$-ml portions of concentrated nitric acid into the flasks in the same manner. Remove the flask from the hot plate and cool. With distilled water, rinse the glass hook and funnel and collect the rinsings in the flask. Then rinse down the flask walls. Bring the digestate to a boil for a few minutes to expel nitrogen oxides and then cool.

Aeration First, determine the blank and establish the cleanliness of the aeration apparatus. Add 10 ml of the 1: 3 sulfuric acid to the gas washing bottle which contains the stirring bar. Bring the volume to 100 ml with distilled water. With the air flow diverted through the bypass and the recorder operating, syringe 2 ml of stannous chloride solution into the gas washing bottle. Immediately insert the bottle into the aeration apparatus and position the stirring motor. Allow the contents to mix for 1 min and then direct the air flow through the bottle. After approximately 3 min, divert the air flow through the bypass and remove the gas washing bottle from the apparatus. Rinse the bottle and the fritted bubbler several times with distilled water. Repeat the blank determination three or four times.

Next, aerate the digested samples. Use a stream of distilled water to quantitatively transfer a digestate into the gas washing bottle which contains 10 ml of 1: 3 sulfuric acid and the stirring bar. Add sufficient distilled water to bring the volume to the 100-ml mark. Then treat the sample solution in the same manner as the blank determination. The mercury content of the sample will be recorded as a peak which is characterized by an immediate rapid rise and a decay to a baseline (Figure 2). After aeration, rinse the bottle as before and transfer the next digestate.

Calculation Measure the height of the peak perpendicular to a baseline drawn in the manner shown in Figure 2, curve B. If necessary, correct the

peak height for the distilled water blank. Using the corrected peak height, read the micrograms of mercury in the sample from the appropriate calibration graph. Calculate the parts per billion of mercury and average the results of the duplicate determinations.

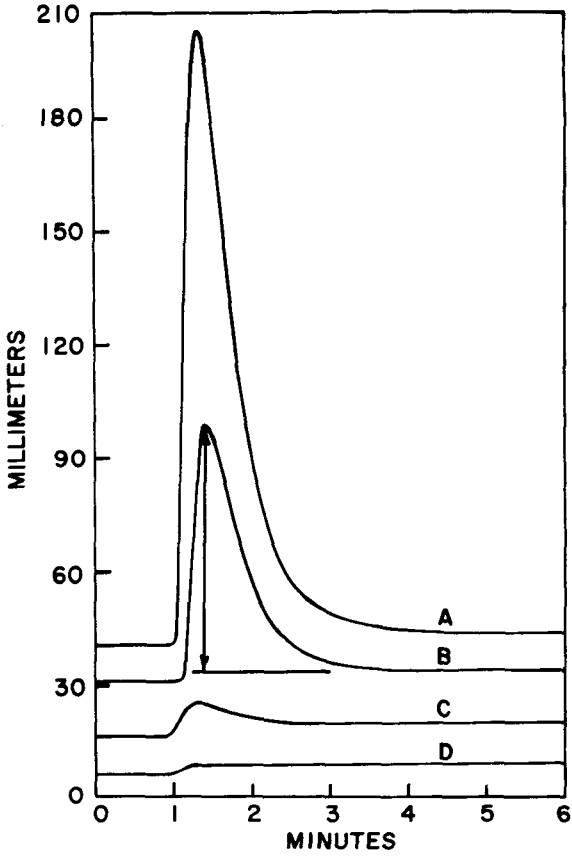

FIGURE 2 Measurement of peak height on typical peaks.
A = 0.5 mcg mercury at 3X
B = 0.07 mcg mercury at 10X
C = 0.006 mcg mercury at 10X
D = blank

DISCUSSION

The procedure has been routinely applied to several hundred samples of raw and treated industrial effluents. Although many of these samples contained unknown amounts and types of organic compounds from manu-

facturing operations, all were easily digested and analyzed for mercury. In addition, the procedure has been applied to municipal and industrial water supplies, and, with minor modification, to numerous proprietary chemicals.

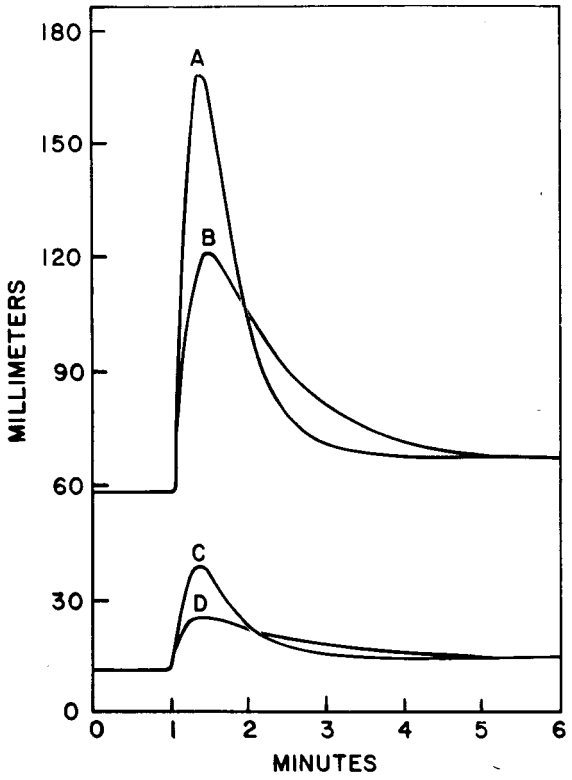

FIGURE 3 Effect of antifoam on peak height.

A = 0.33 mcg mercury
B = 0.33 mcg mercury with antifoam
C = 0.075 mcg mercury
D = 0.075 mcg mercury with antifoam

Some typical peaks obtained during analysis, together with the technique for measuring peak height, are shown in Figure 2. On the chart, the final baseline is extended to the front of the peak and the peak height is measured perpendicular to this line. At scale expansions of 3X and 10X, the peak height in millimeters is approximately proportional to absorbance and may be used as the ordinate on the calibration graph. For samples containing large amounts of mercury, the peak is recorded on the normal 1X setting. Then the

peak height is measured in per cent absorption which is then converted to absorbance.

In the digestion, concentrated sulfuric acid and nitric acid are added to the effluent. An antifoam agent is added to prevent foaming and possible boiling over as the water is evaporated. Dow Corning Antifoam H-10 Emulsion was selected for this purpose because it is stable in hot, acidic aqueous solutions. The antifoam is effective as long as water is present in the flask; then the antifoam is digested together with the other organic matter. As a result, it does not affect the measurement of mercury in the aeration step. The effect of organics on the aeration may be seen in Figure 3, which shows the results of adding three drops of H-10 antifoam agent (diluted 1 : 9) to calibration solutions. With organics present, the air passes through the solution in very large bubbles and a longer scrubbing time is required to remove the mercury from the solution. This results in a flattened peak and a reduction in sensitivity. To obtain a tall, sharp peak on the chart, the bulk of the mercury should be transported through the cell in the initial volume of air. This can be accomplished by dispersing the air as fine bubbles in the solution.

Near the end of the digestion, carbonization of the organic matter will darken the solution as the digestate is reduced to sulfuric acid fumes. Through careful addition of small amounts of concentrated nitric acid each time the digestate begins to darken, the loss of mercury by carbon reduction is prevented. The digestate will remain clear when all organic matter has been destroyed. Although digestions in Erlenmeyer flasks have yielded satisfactory results, the procedure can easily be adapted to a Bethge apparatus.

The absence of interfering organic matter in the digestate was verified by the analysis of proprietary chemicals. As an example, eight individual portions of a latex emulsion were digested. Four of these digestates, selected at random and aerated in the normal manner, yielded identical peaks. When the four remaining digestates were aerated with the aeration apparatus modified by placing a $1\frac{1}{2}$-in. long tightly rolled silver screen plug in the heated line, no peaks were obtained on the recorder chart.

To ascertain that organomercurial compounds are decomposed and that the mercury is recovered, four compounds were digested and analyzed in triplicate. These compounds were phenylmercuric acetate, pyridylmercuric acetate, pyridylmercuric stearate, and di(phenylmercuric)dodecenylsuccinate. The first three were technical-grade products and the last compound, which contains 47.9% mercury, comprised 21% of Super Ad-It, a liquid fungicide additive for paints. From the stated mercury content, a calculated amount of a material was weighed into flasks so that each flask contained 100 mg of mercury. These samples were digested, appropriately diluted, and analyzed. Although the materials were of technical-grade quality, the data given in

Table I show that mercury can be recovered from organic compounds. The results for the three solid compounds are slightly high because of the non-homogeneity of these technical-grade products and a low stated assay. There was no evidence that any residual amounts of interfering organics, such as phenyl or pyridyl compounds, were present during measurement of the mercury.

TABLE I

Recovery of mercury from organomercurial compounds

Compound	Mercury (mg)	
	Taken	Found
Di(phenylmercuric)dodecenylsuccinate	100	101
	100	96
	100	105
Pyridylmercuric stearate	100	104
	100	120
	100	103
Phenylmercuric acetate	100	107
	100	116
	100	110
Pyridylmercuric acetate	100	112
	100	113
	100	121

The digestion procedure was applied to prepared samples containing 1, 5, and 10 ppb ionic mercury. These samples were prepared by dissolving 0.1000 g of metallic mercury in a minimum amount of nitric acid and then serially diluting with distilled water to obtain solutions with the final desired concentrations. The digestion procedure was carried out on 100-ml portions of the final solutions and the mercury was measured. The recoveries of mercury, given in Table II, show that ionic mercury is retained in the digestate.

Similarly, the recovery of mercury from five different effluents was studied. These effluents, which originated at different industrial locations, contained different amounts and types of soluble and particulate organic matter. Weighed 100-ml portions of each effluent were spiked by pipetting a known volume of an ionic mercury solution into each Erlenmeyer flask. To correct for any mercury that may have been present originally, duplicate 100-ml portions of each unspiked effluent were taken in separate flasks. All samples

TABLE II

Recovery of ionic mercury from solution

Sample	Mercury (ppb)	
	Taken	Found
A	1.0	1.1
B	1.0	1.0
C	1.0	1.4
D	5.0	5.0
E	5.0	5.0
F	5.0	5.0
G	10.0	10.0
H	10.0	10.0

TABLE III

Recovery of mercury from effluents

Effluent	Mercury (ppb)	
	Added	Recovered
A	1.0	1.1
	1.0	0.9
	1.0	1.0
B	1.0	1.0
	1.0	1.0
	1.0	1.1
	1.0	1.1
C	1.0	1.0
D	1.0	1.0
	1.0	0.9
E	5.0	4.9

were then digested and analyzed according to the procedure. The results, given in Table III, show that the presence of various unidentified organic compounds in the effluents has no effect on the recovery of mercury from the effluents.

Many proprietary chemicals in use today in industry may contain mercury. The mercury is present either as a residue from the preparative process or as an organomercurial compound added for fungicidal or bactericidal purposes. Various proprietary chemicals, such as latex, vinylpyridine, dye, stain, sizing, hydro, and caustic have been analyzed satisfactorily with the procedure (Table IV). Generally, these materials do not contain gross amounts of water,

TABLE IV

Analysis of proprietary chemicals

Chemical	Mercury (ppb)
Latex	15, 14
Latex	25, 28
Vinylpyridine	210, 220, 214
Vinylpyridine	7, 7
Rayon Dye	409, 410
Stain	184, 184
Sizing	0, 0
Hydro	0, 0
Caustic	24, 22
Caustic	19, 17

and the use of the antifoam agent can be omitted. To digest a proprietary chemical such as latex, triplicate 2-g portions are weighed into 125-ml Erlenmeyer flasks. Before placing the glass hook and funnel in the flask neck, 6-ml of concentrated sulfuric acid and 3-ml of concentrated nitric acid are added to each flask. With many samples, digestion begins immediately upon addition of acid and must be controlled by intermittent immersion of the flask in a cold water bath. Other samples may require a brief, gentle warming to initiate the digestion process. Incremental addition of concentrated nitric acid must be started immediately in order to minimize charring of organics and prevent loss of mercury. When the digestate remains clear, complete the digestion as with the effluents. Caustic samples do not require digestion unless the presence of organic substances is suspected. However, careful neutralization of the caustic with concentrated sulfuric acid is required before analysis or digestion.

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