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Chemistry

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DETERMINATION OF SUBMICROGRAM QUANTITIES OF MERCURY IN WATER AND LITHIUM HYDROXIDE SOLUTIONS

M. S. Dill

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ABSTRACT

A method has been developed for determining submicrogram quantities of mercury in water and lithium hydroxide. The detection limit is 2×10^{-4} micrograms per milliliter. The mercury is reduced to metal and then expelled from a solution as vapor. The vapor is measured using an atomic absorption spectrophotometer.

CONTENTS

SUMMARY

An atomic absorption spectrophotometric method for determining submicrogram amounts of mercury has a detection limit of 2×10^{-4} µgs/ml and a precision of ± 10 percent at the 2×10^{-3} µgs/ml level, when based upon a 50-milliliter sample. The total mercury content of an aliquant must be less than one microgram for the determination by this method.

The method consists of: (1) converting the mercury ions to the metal, (2) expelling the metallic mercury as the vapor, and (3) measuring the vapor in an absorption cell. Time required for an analysis is approximately five minutes per sample.

The only interferences found were vapors which absorb at 2537 A and metallic ions which are reduced to the metal and form an alloy with the metallic mercury.

INTRODUCTION

The Biology Division of the Oak Ridge National Laboratory asked that some water samples be analyzed to see if the mercury concentration exceeded 1×10^{-2} µgs/ml. A new method had to be found because the lower limit of the mercurometer was 5×10^{-2} µgs/ml; the colorimetric procedure(1) was too time consuming.

Several papers on mercury analysis by atomic absorption have been published, (2) but most of these methods require a solvent extraction of the mercury ion into an organic phase to concentrate the mercury before atmoizing into the flame. These methods are often inadequate because: (1) mercury in the water is usually in the metallic form, and (2) extraction does not concentrate the mercury sufficiently, if one is interested in submicrogram quantities.

Russian workers published an article on the analysis of mercury in the gas phase using atomic absorption(3). This principle, adapted to the Laboratory's samples and equipment, was utilized in developing the present method of determining submicrogram quantities of mercury in water and in lithium hydroxide solutions.

METHOD FOR MERCURY DETERMINATION

REAGENTS AND EQUIPMENT

Reagents

The following reagents are required:

Stannous Chloride Solution, 20% - Dissolve 20 grams of CP tin(II) chloride dihydrate in 100 milliliters of 6 normal hydrochloric acid.

Mercury Solution, 100 µgs/ml - Dissolve 108 milligrams of mercury(II) oxide in 50 milliliters of 5 normal nitric acid. Dilute with water to the mark in a 1000-milliliter volumetric flask.

Mercury Solution, 0.1 µgs/ml - Pipette one milliliter of the standard mercury(II) oxide solution (100 µgs/ml) into a 1000-milliliter flask and dilute with 0.25 normal nitric acid to the mark.

Equipment

The following major items of equipment are needed: an atomic absorption spectrophotometer(a) equipped with a recorder readout, and an absorption cell and reaction train (see Figure 1).

RECOMMENDED PROCEDURE

Preparation of Standards

The standard solutions should be prepared as follows:

1. Pipette the mercury standard solution (0.1 µgs/ml) into the reaction flasks in known amounts to give a series of five standards to cover the expected range of samples. (The highest standard that can be used is 1.0 µg Hg total.)
2. Dilute the standard solution in the reaction flask to a 50-milliliter volume.

(a) Model 303, Perkin-Elmer Corporation.

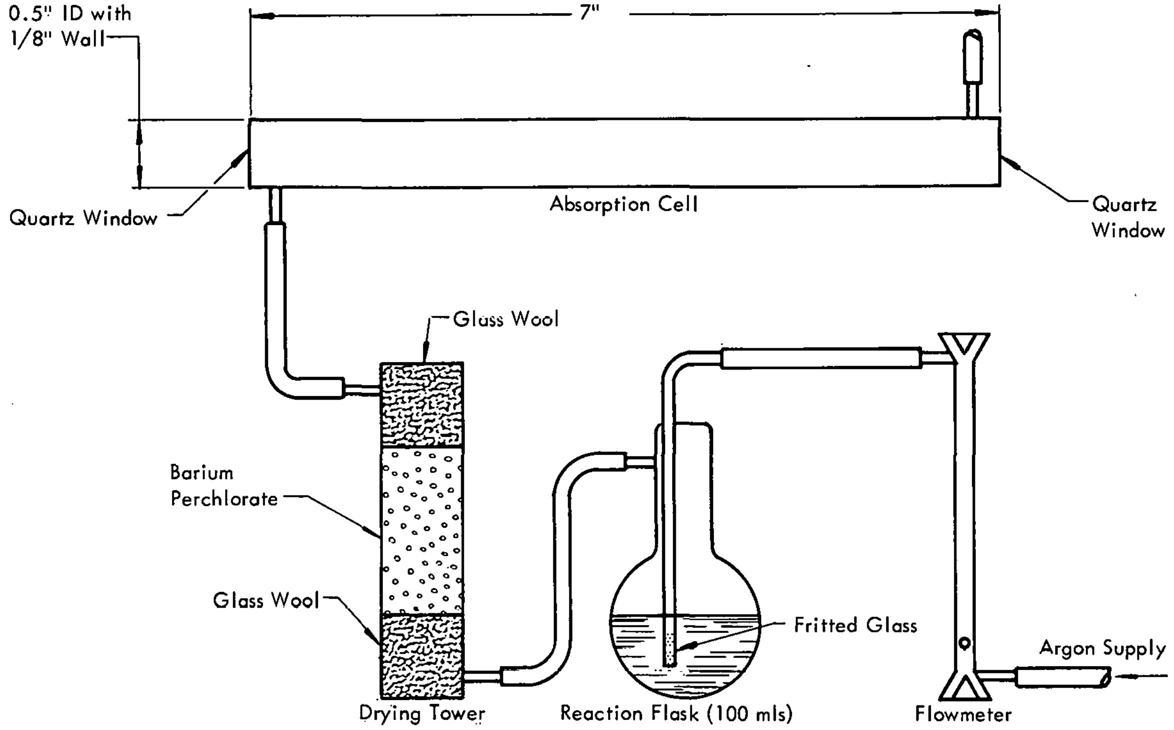

Figure 1. MERCURY ABSORPTION CELL AND REACTION TRAIN.

3. Add 0.5 milliliter of tin(II) chloride solution to each reaction flask. Stopper the flask and invert five times to provide thorough mixing.
4. React the standard within ten minutes after the addition of the tin chloride.

Preparation of Samples

Samples should be prepared as follows:

1. Pipette into the reaction flask a portion of sample which gives a total mercury value corresponding to the standard curve.
2. If the sample is basic, add nitric acid until the pH is less than 7.
3. Dilute the sample in the reaction flask to a 50-milliliter volume.
4. Add 0.5 milliliter of tin(II) chloride solution to the reaction flask. Stopper the flask and invert five times to provide thorough mixing.
5. React the samples within ten minutes after the addition of the tin chloride.

Analytical Procedure

The analysis for mercury should be conducted according to the following procedure:

1. Remove the burner from the instrument and install the mercury absorption cell.

2. Align the absorption cell to obtain maximum intensity of the mercury source lamp through the cell.

3. The instrument operating conditions are:

   Source Lamp - mercury germicidal
   Lamp Current - 350 milliamperes
   Slit Width - 3 (0.3 mm)
   Wavelength - 2537 A
   Noise Control - 1
   Scale Expansion - 1X
   Gain Control - 2.5
   Argon Flow - 2.0 liters per minute (at 760 mm and 24° C)

4. Adjust the recorder to zero absorbance, then insert the gas dispersion adapter into the reaction flask and allow it to remain until the recorder returns to zero absorbance.

5. Compare the sample absorbance data to the absorbance data of the standards to obtain the total micrograms of mercury in the reaction flask.

6. Calculate the results by the following equation:

$$\mu\text{gs Hg/ml} = \frac{\text{Total } \mu\text{gs Hg Found in Reaction Flask}}{\text{mls of Sample Used}}.$$

EXPERIMENTATION

Synthetic samples were prepared by adding mercury(II) nitrate to water and lithium hydroxide solutions. The lithium hydroxide concentration was approximately 2.5 mgs Li/ml. Typical results of these experiments are summarized in Table 1.

Table 1

ANALYSIS FOR MERCURY IN WATER AND LITHIUM HYDROXIDE SOLUTIONS

Sample Number	Total Mercury Added (µg)	Total Mercury Found (µg)	Actual Mercury Value (in µgs Hg/ml)	Mercury Value Obtained (in µgs Hg/ml)
Water				
1	0.100	0.100	0.002	0.00200
2	0.100	0.095	0.002	0.00190
3	0.100	0.098	0.002	0.00196
4	0.100	0.105	0.002	0.00210
5	0.100	0.095	0.002	0.00190
6	0.100	0.100	0.002	0.00200
7	0.100	0.106	0.002	0.00212
8	0.100	0.098	0.002	0.00196
9	0.100	0.103	0.002	0.00206
10	0.100	0.101	0.002	0.00202
Lithium Hydroxide				
1	0.4750	0.470	0.0475	0.0470
2	0.4750	0.475	0.0475	0.0475
3	0.4750	0.475	0.0475	0.0475
4	0.4750	0.490	0.0475	0.0490
5	0.4750	0.480	0.0475	0.0480
6	0.4750	0.475	0.0475	0.0475
7	0.4750	0.465	0.0475	0.0465

RESULTS AND DISCUSSION

Atomic absorption analysis of mercury in the vapor phase in an absorption cell has the following advantages over the burner method: (1) all of the mercury is in the zero energy state; (2) there is no interference from burning conditions; (3) there is no flame "noise"; and (4) very low detection limits can be reached. The disadvantages are that: (1) samples may contain organic vapors which absorb at 2537A giving false readings, and (2) metallic ions may be present which would be reduced to the metal with tin(II) chloride that would then be alloyed with the mercury to prevent it from being expelled from the solution. Metals known to interfere are gold, platinum, selenium, and tellurium.(4)

The presence of organic vapors that absorb in the 2537 A region can be detected by the response of the chart recorder, as shown in Figure 2. The failure of the recorder pen to return to zero absorbance indicates that an absorbing vapor is being expelled at a constant rate. Several organics that absorb at 2537 A were tested but none were found that expelled as quickly as possible. All reacted similarly to acetone, shown in Figure 2.

The samples can be checked for the interference of metallic ions by spiking with mercury and checking the recovery. Failure to recover the spike indicates interfering metallic ions.

The glass frit in the reaction tube is necessary to produce a fast and constant rate of expelling the mercury vapor. An open-end tube was found unsatisfactory for use.

It is necessary to dilute the samples and standards to the same volume. The gas flow rate must be held constant since this determines the rate at which the mercury is expelled and the number of atoms in the absorption path at any given time.

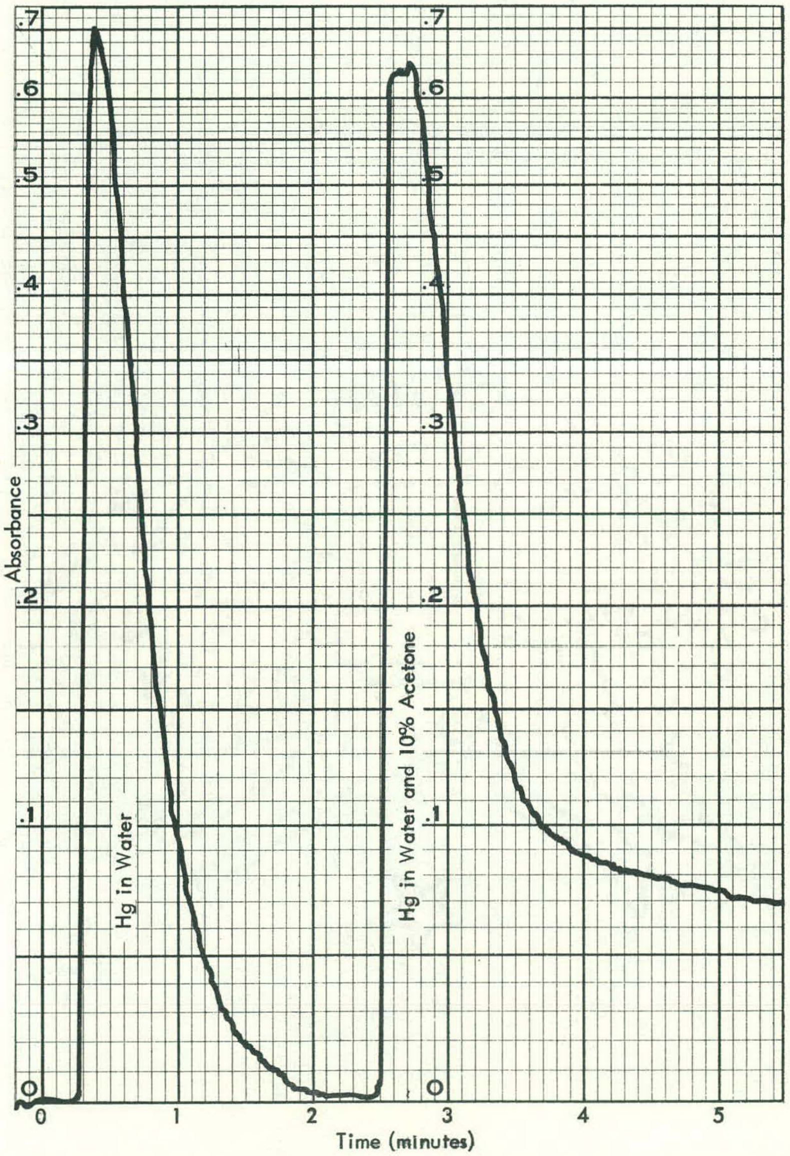

Figure 2. EFFECT OF ORGANIC VAPORS ON ABSORBANCE.

The concentration of sulfuric, nitric, and perchloric acids and mixtures of these acids did not affect the results below five normal. Above this concentration, nitric acid will decompose and release fumes which will absorb, giving false readings.

To obtain total absorbance of a sample, an integrating recorder was tried and found to be unnecessary because of the fast and constant rate at which the mercury vapor was expelled (see Figure 3).

The absorption cell was designed to give the greatest absorption at optimum conditions. The important parameters are: (1) focal distance of the reflecting mirror, (2) gas flow rate, (3) intensity of the source light, (4) detection limit needed, and (5) sample reaction time.

Barium perchlorate was chosen for the drying agent because of its high absorbing power for water.

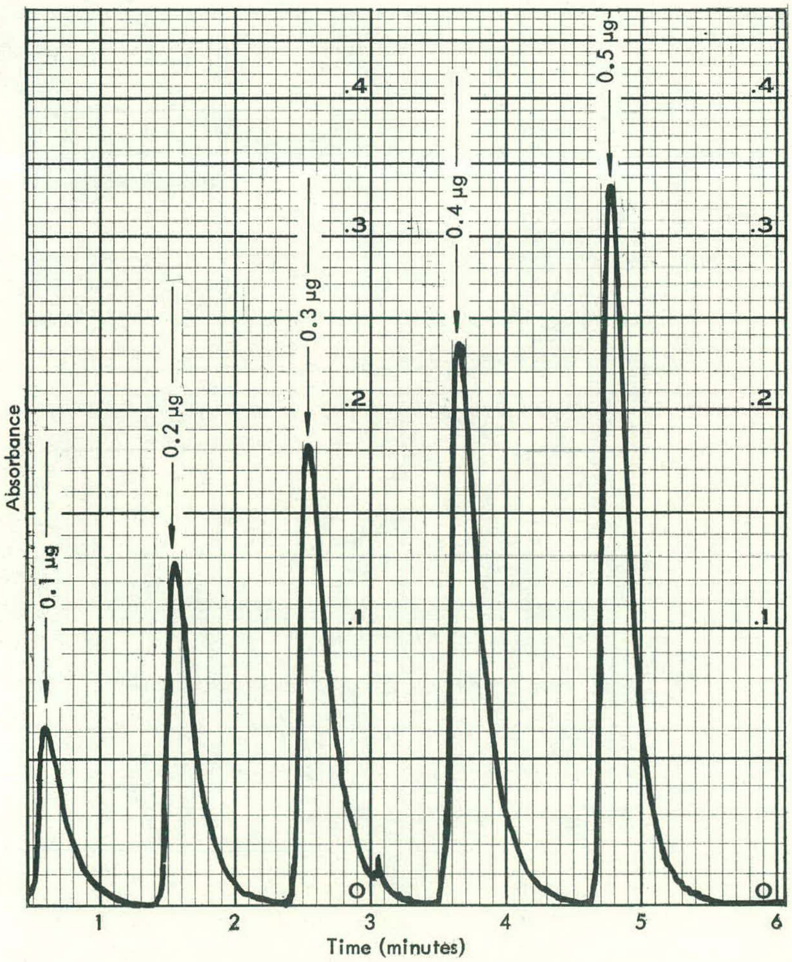

Figure 3. ABSORBANCE PEAKS FOR VARIOUS MERCURY STANDARDS SOLUTIONS.

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