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DETERMINATION OF MERCURY IN RADIOACTIVE SAMPLES BY FLAMELESS ATOMIC ABSORPTION SPECTROPHOTOMETRY

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DETERMINATION OF MERCURY IN RADIOACTIVE SAMPLES BY FLAMELESS ATOMIC ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

A flameless atomic absorption technique was adapted for the determination of mercury in highly radioactive samples. Mercury is isolated on a small copper coil by spontaneous displacement from acid solution and is then vaporized by resistance heating in an evacuated cell in the light path of an atomic absorption spectrophotometer. The mass of mercury vapor is determined by attenuation of characteristic mercury radiation. Concentrations of mercury as low as 10^{-5}M in solutions containing as much as 10^{12} d/(min)(ml) of alpha activity and 10^{12} c/(min)(ml) of beta-gamma activity were determined with precisions of about 5%. The method was used successfully to trace the path of mercury in plant processes and to determine the concentration of mercury in plant product.

INTRODUCTION

Mercury is frequently used at the Savannah River Plant and Laboratory as a catalyst in the one-step dissolution of irradiated target elements and consequently is found in many process streams. The removal of mercury from plant products has not been unusually difficult, although trace levels of mercury sometimes persist. In many of the separations processes, mercury is largely extracted into the organic streams. If the solvent is to be recycled through the process, the mercury is removed to prevent its buildup to troublesome concentrations. Mercury analyses are frequently required to define product quality and to trace the path of mercury during processing.

Emission spectrographic techniques for mercury analysis usually lack sensitivity because of the extreme volatility of mercury and its consequently short residence time in the arc. Even spark source mass spectrometric techniques suffer from the same defect. The dithizone colorimetric method(1) is sufficiently sensitive, but involves tedious sample preparation and suffers interference from a number of chemical species frequently present.

Conventional atomic absorption, with a flame-type absorption source, is relatively sensitive, although the sensitivity is greatly influenced by the presence of chemical species that may complex mercury.(2) The analysis of highly radioactive samples with a conventional, uncontained atomic absorption spectrophotometer requires that the samples be diluted or decontaminated to reduce the radioactivity to a safe level for injection into the flame. The mercury concentration in many samples of present interest was too low to permit the necessary dilution, and the chemical decontamination procedures attempted resulted in erratic losses of mercury.

Brandenberger and Bader(3) recently described a flameless atomic absorption technique for mercury analysis, which appeared to offer high sensitivity and the potential for the required decontamination. This report describes the adaptation and application of their method.

PROCEDURE

In the flameless atomic absorption analysis, mercury is isolated from a 0.1M nitric acid solution of the sample by amalgamation onto a 40-cm length of No. 38 copper wire wound into a coil about 1/4 inch in diameter and 3/4 inch in length. While the amalgamation can be conducted electrolytically in appreciably less time, the spontaneous deposition procedure was adopted for the present application because its greater selectivity provided higher decontamination from radioactive species. The spontaneous amalgamation is accomplished by submerging a coil in the stirred sample solution for three hours. As shown in Figure 1, almost all of the mercury is removed from the solution within this period. After thorough washing with distilled water, alcohol, and acetone, the coil is dried, mounted in the holder shown in Figure 2, and positioned in the side arm of the absorption cell shown in Figure 3. The absorption cell is located in the light path of the atomic absorption spectrophotometer.

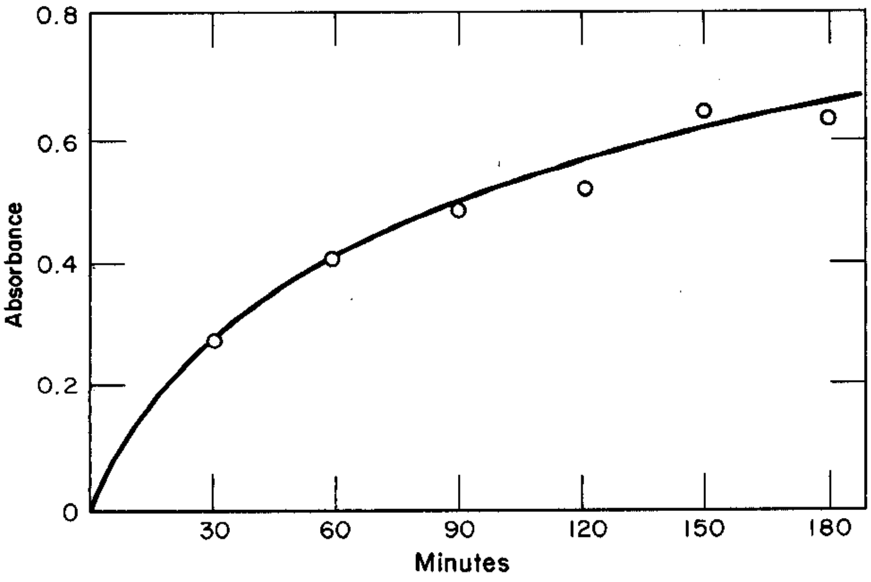
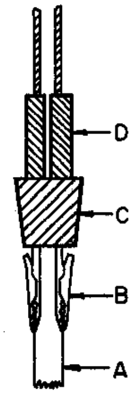
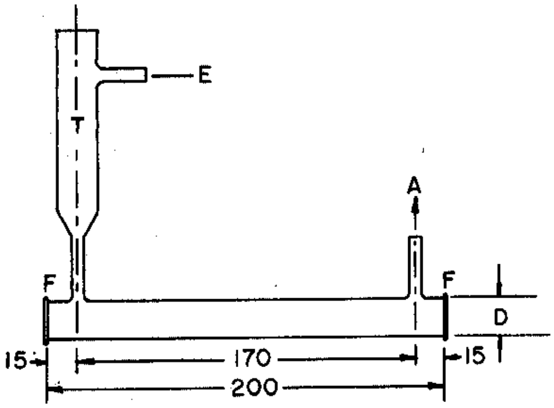


FIG. 1 SPONTANEOUS DEPOSITION OF MERCURY FROM 0.1M HNO_3 ON A COPPER WIRE (Reproduced from Reference 3)



A = Copper Wire
B = Alligator Clamps
C = Rubber Stopper, Two-hole
D = Banana Plug

FIG. 2 SUPPORT FOR COPPER COIL
(Reproduced from Reference 3)



T = Funnel for Introducing Copper Wire
E = Air Inlet Tube
A = Air Outlet Tube
F = Quartz Window of Diameter D
Dimensions in mm

FIG. 3 ABSORPTION CELL FOR ANALYSIS OF MERCURY VAPOR
(Reproduced from Reference 3)

The mercury is determined by attenuation of 2537A radiation from a mercury vapor lamp after volatilization from the copper coil by resistance heating. Either a dynamic or static procedure can be used. With the dynamic method, a constant flow of gas is established through the absorption cell, and as the mercury is vaporized and passed through the cell, the absorption is measured as a function of time. The mass of mercury is proportional to the peak absorbance. With the static method, which was used in the present studies, the cell is evacuated, and the mercury is vaporized for measurement of total absorbance. The proportionality between absorbance and mass of mercury is determined with standard samples. The relationship is linear from 2 to 200 ng of mercury.

The flameless atomic absorption analysis for mercury is about 10^4 times as sensitive as the conventional flame technique; the detection limit is 0.2 ng of mercury. The precision is about 10% in the 0.2 to 10 ng range, and about 5% in the 10 to 200 ng range.

Metals that are not displaced from solution by copper, such as uranium, aluminum, sodium, and lithium, do not interfere with the analysis even when present in high concentrations. Metals that are displaced by copper, such as silver, apparently do not interfere with the amalgamation but may interfere with the subsequent measurement. When silver was codeposited with mercury, some silver was apparently carried off with the burst of mercury when the coil was heated; this silver deposited on the cell walls, where it absorbed mercury and caused erroneous results. This interference was eliminated by adding sodium chloride to the sample solution to complex the silver and prevent its displacement by copper.

Mercury must be present in ionic form in order to be spontaneously deposited on copper from solution. Thus, mercury in organic systems cannot usually be analyzed directly. Satisfactory analysis of mercury in a diethylbenzene-tertiary amine extractant was accomplished by stripping the mercury from the extractant with 2.5M K_2CO_3—0.13M EDTA, and analyzing the strip solution after acidifying it to 0.1M HNO_3.

APPLICATIONS

The exceptionally high sensitivity of the flameless atomic absorption technique has greatly facilitated the analysis of mercury in highly radioactive samples. The high sensitivity permits the use of very small samples; this, together with the decontamination inherent in the amalgamation step, allows the absorbance measurements to be made without elaborate containment facilities. As an example, mercury in a solution containing 10^{12} d/(min)(ml) alpha (actinide) activity and 10^{12} c/(min)(ml) beta-gamma (fission product) activity was analyzed after diluting a small aliquot of the solution by a factor of 10^4 to 10^5 to reduce the radioactivity to a level that can be safely handled in a well-ventilated hood. After deposition of the mercury, no alpha activity was detected on the copper coil. A decontamination factor of about 10^6 to 10^7 was obtained for beta-gamma activity, the limit being imposed by codeposition of ruthenium on the coil.

This new analysis for mercury has been used successfully in the following applications at the Savannah River Laboratory:

- To determine the concentration of mercury in ^{244}Cm process solutions and to trace the path of mercury in the Tramex process.(4)
- To determine the effectiveness of techniques for diverting mercury to waste in the Tramex process, and to verify that mercury was not accumulated in the solvent extractant.
- To determine the concentration of mercury in ^{235}U, ^{233}U, and ^{237}Np processed at the Savannah River Plant.

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THE DETERMINATION OF NANOGRAM LEVELS OF MERCURY IN SOLUTION BY A FLAMELESS ATOMIC ABSORPTION TECHNIQUE*

by
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ABSTRACT

A flameless atomic absorption method for the determination of small amounts of mercury in solution is described. The mercury is amalgamated quantitatively on a copper wire and subsequently vaporized in an absorption cell which is placed in the light path of a commercial atomic absorption instrument. The mercury vapor can be quantitatively determined by its absorption of the 253.7 mercury line. The method has a detection limit of 0.2 nanogram (ng) and is therefore about 10,000 times more sensitive than atomic absorption analysis using flame atomization.

RESUME

Une méthode pour la détermination de petites quantités de mercure inorganique en solution, par absorption atomique sans flamme est décrite. Le mercure est amalgamé quantitativement sur un fil de cuivre et évaporé ensuite dans une cellule d'absorption placée dans le trajet du rayon lumineux d'un instrument commercial d'absorption atomique. Le mercure vaporisé est dosé par son absorption caractéristique à 253,7 nm. La limite de détection est de 0,2 ng; la sensibilité de cette méthode est donc d'environ 10,000 fois plus grande que celle du dosage effectué avec atomisation par flamme.

ZUSAMMENFASSUNG

Ein flammenloses atomares Absorptionsverfahren für die Bestimmung von kleinen Mengen anorganischem Quecksilber in Lösung ist beschrieben. Das Quecksilber wird quantitativ an einer Kupferspirale amalgamiert und anschliessend in einem im Strahlengang eines kommerziellen atomaren Spektrophotometers befindlichen Absorptionsrohr verdampft. Die entstehende Quecksilberdampfwolke wird anhand ihrer Absorption der Quecksilberlinie bei 253,7 nm bestimmt. Die Methode kann noch 0,2 ng Quecksilber erfassen; sie ist 10,000 mal empfindlicher als atomare Flammenabsorptionsanalyse.

A method has been developed for producing from solution a cool atomic vapor of mercury that can be determined by a commercial atomic absorption spectrophotometer. The mercury is amalgamated from solution on a copper wire which is then electrically heated to vaporize the mercury in an absorption cell placed in the light beam of the spectrophotometer. The mercury vapor, while being pumped through the cell, absorbs radiation from a mercury vapor lamp. The resulting absorption is plotted as a function of time by a recorder.

The deposition of metals such as silver, mercury, arsenic, antimony and bismuth on copper is still recommended (1) in the form of the Reinsch test (2) for the qualitative detection of these elements in biological materials. The specimens to be analyzed are heated in hydrochloric acid solution in the presence of a piece of sheet copper. The first two of the metals listed for this test produce a metallic luster, the others a black coating on the copper. A few μg of mercury are needed for this simple test. Dal Cortivo et al (3) deposited mercury from solution on copper powder and analyzed it in an emission spectrograph. With this method, 0.5 μg of mercury can be detected. We have chosen to amalgamate on a 0.1 mm copper wire so the mercury can readily be vaporized by ohmic heating. To deposit 100 ng of mercury quantitatively would require 150 to 200 min (Fig. 1). By applying a 3 V potential the time needed is reduced to one-tenth as much.

The deposited mercury is vaporized by applying a 5 V potential to heat the copper wire after placing it in the side arm of an absorption cell. The dimensions of the absorption cell are chosen so it can be placed in the light beam of the spectrophotometer. The absorption cell, used with a Perkin-Elmer Model 303 spectrophotometer, is shown schematically in Fig. 2. The cell and side arm are

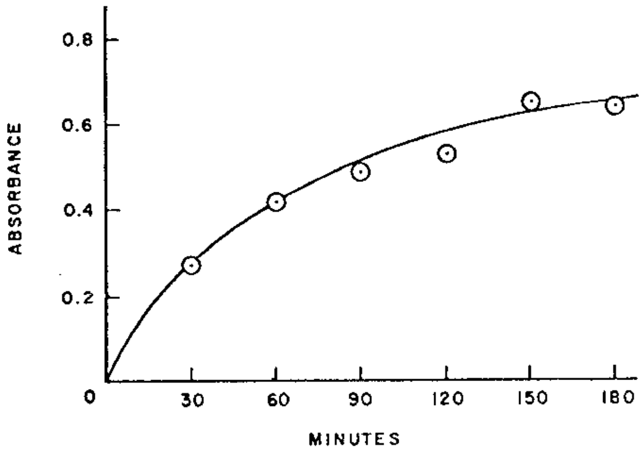

Fig. 1. Spontaneous Amalgamation of 135 ng Hg from 0.1 N HNO_3 on a Copper Wire.

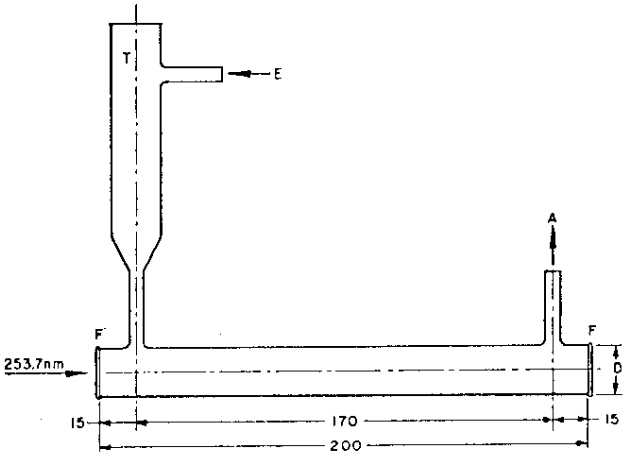

Fig. 2. Absorption Cell for Absorption of Mercury Vapor
T = Funnel for introducing copper wire
E = Air inlet tube
A = Air outlet tube
F = Quartz window of diameter D
Dimensions in mm.

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*Slightly abbreviated translation from Helvetica Chimica Acta 50, 1409-1415 (1967), with special permission of the editorial board.

glass, with fused quartz windows at the ends of the cell. Figure 3 shows how the copper wire is supported by the stopper C, which also provides entry into the funnel T of the absorption cell.

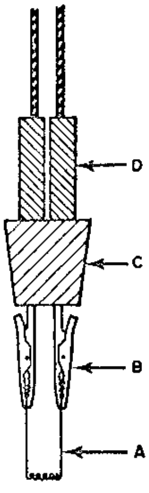

Fig. 3. Support for the Copper Wire
A = Copper wire
B = Alligator clamps
C = Rubber stopper, two-hole
D = Banana plug

For the determination of the mercury atoms either a static or a dynamic process may be used. With the static method the cell is evacuated, the mercury allowed to vaporize, and the mass of the mercury vapor determined by absorption in a beam of mercury radiation. With the other method a constant gas flow is established in the absorption cell and the mercury atoms are drawn through the cell. Absorption of the radiation is then recorded as a function of time. Thus far we have used only the dynamic method of measurement, leaving the static type for future work.

EXPERIMENTAL

A 0.1 mm diameter copper wire 400 mm long was formed into a 10 to 15 mm long coil on a 4 mm thick glass rod, with leads about 20 mm coming off each end in the same direction. The leads were held by two alligator clips on a banana plug supported in a two-hole rubber stopper (Fig. 3). Just before use the copper wire was cleaned by dipping it in 30% nitric acid and rinsing with distilled water. For electrolytic deposition the copper wire was used as cathode, the anode being a coil of 1.0 mm platinum wire 70 mm long. The electrolysis took place in a 5-ml PVC beaker 20 mm in diameter and 16 mm high. Mixing was carried out with a magnetic stirrer. At an electrode potential of 3 V (10 to 15 ma current) up to 150 ng of mercury was deposited within 20 min from solution with 1 to 20 ppb saliniform mercury in 0.1 N HNO_3. After electrolysis the copper wire was washed with distilled water, alcohol and then acetone.

To atomize the mercury, the copper wire was positioned in the funnel T of the absorption cell (Fig. 2) and, after the cell was placed in the light beam of a Perkin-Elmer Model 303 spectrophotometer, heated by 5 V DC or AC. The deposited mercury was vaporized instantaneously. A current of air produced by a water pump drew the mercury vapor through the absorption cell. The speed of the air stream was adjusted to provide an average transit time through the cell of 4.6 sec. Absorption of radiation from a Westinghouse mercury vapor lamp transmitted through the cell was recorded as a function of time on a 10 mV Sargent recorder, which can provide either a logarithmic or linear output depending on whether scale expansion is used. For either type the recorded signal depends linearly on the mercury concentration. The spectral measurement was made at 253.7 mμ with a spectral slit width of 2A (Setting 3). The mercury vapor arc current was 300 ma.

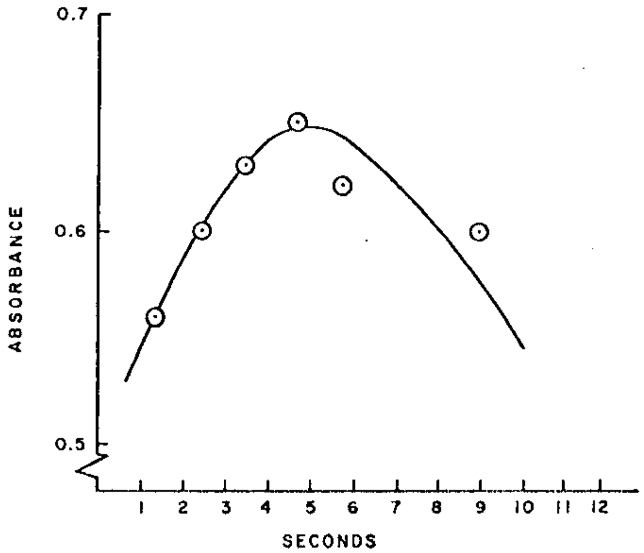

Fig. 4. Effect of Transit Time on Absorption in the Determination of 135 ng Hg.

Both the cell diameter and the speed of the gas flow are of critical importance for the magnitude of the absorption. Figure 4 shows that a transit time of 4.6 sec. gives the best results. The effect of the cell diameter is shown in Table I. The lower limit for the diameter is given by the approximately 16 mm breadth of the light beam in the spectrophotometer. Two comparison measurements for cells of 18 and 20 mm diameter are given in Fig. 5.

TABLE I
Effect of the Absorption Cell Diameter D on the Sensitivity

D (mm)	56	28	20	18
$\pi(D/2)^2$ (mm^2)	2460	615	314	254
ng Hg/0.1 E	200	54	20	18

RESULTS

The spectroscopic measurement was carried out at 253.7 nm, with the same conditions as employed for mercury in flame atomic absorption (see the Experimental Section). The measured values in Figs. 4 and 5 and in Table I were produced without the use of scale expansion. An ordinate scale expansion may be used and makes possible a detection limit of 0.2 ng mercury. Table II shows the quantitative capability with and without scale expansion. In comparison with flame atomic absorption, the sensitivity of our method is about 10,000 times greater. The range of linearity is 10^3 (0.2 to 200 ng). Figure 6

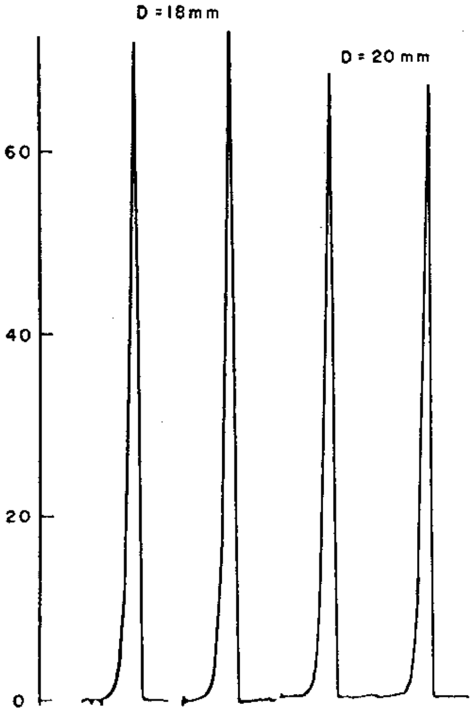

Fig. 5. Two Determinations of 132 ng Hg in Absorption Cells of Diameter 18 mm (left) and 20 mm (right), Logarithmically Recorded without Scale Expansion.
Abscissa = Time axis.
Ordinate = Absorption values between limits E = 0.000 and E = 1.000 corresponding to the 0 to 100 scale. Average values of E for each pair of determinations are 0.730 for the 18 mm cell and 0.660 for the 20 mm cell.

TABLE II
Concentration Range and Detection Limits with and without Scale Expansion

Scale Expansion	*ng Hg for 1% Full Scale Deflection*	*Concentration Range in ng Hg*	*Detection Limits ng Hg*	*Reproducibility %*
None	2	2 - 200	2	±3
10X	0.1	0.2 - 10	0.2	±10

shows a working curve for mercury determination between 10 and 200 ng, from a logarithmic recorder without scale expansion. Figure 7 shows a working curve for mercury below 10 ng, with tenfold scale expansion, linear recording. With our measurement technique the heights of the sharp peaks can be compared for quantitative evaluation; integration of areas is not required.

Exploratory investigations using the method for the determination of mercury in urine have yielded satisfactory results. Inorganic material can be deposited directly from urine on copper, avoiding thereby an inconvenient decomposition process with a probable loss of mercury. We have not yet checked the method with organic compounds containing mercury.

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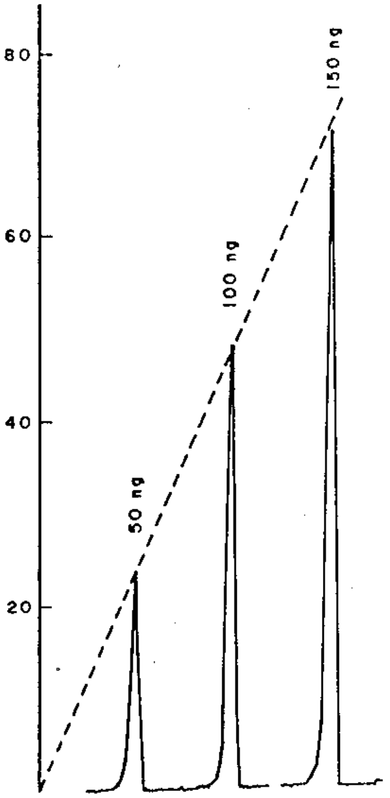

Fig. 6. Calibration Curve for Mercury from 10 to 200 ng, Logarithmically Recorded without Scale Expansion. Abscissa = Time axis; Ordinate = Absorption values between the limits E = 0.000 and E = 1.000, corresponding to the 0 to 100 scale.

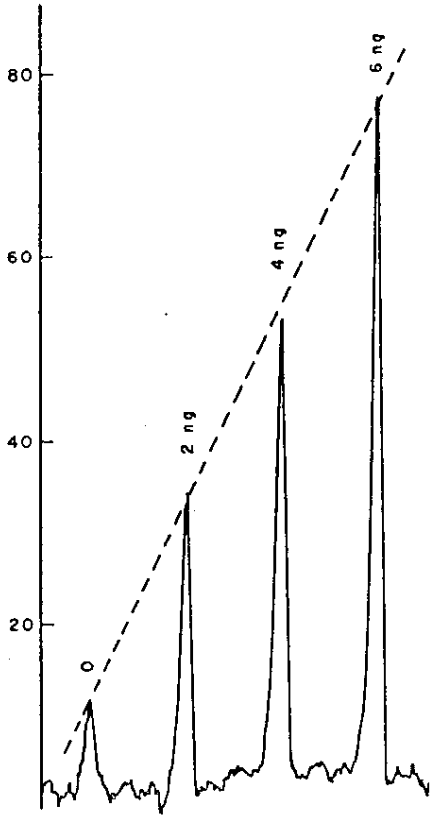

Fig. 7. Calibration Curve for Mercury up to 10 ng, Recorded with Absorption at 10X Scale Expansion. Abscissa = Time axis; Ordinate = linear absorption values between the limits 0% and 10% absorption (corresponding to the 0 to 100 scale). The zero is offset due to mercury in the nitric acid.