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The Determination of Hg-202 and Other Mercury Isotopes in Samples of
Mercury Vapor by Mercury Resonance Radiation Absorbiometry*

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Abstract

A method is described for the determination of the percentage of Hg-202 present in small samples of mercury. An electrodeless discharge tube containing Hg-202 is used as a source of the Hg-202 hyperfine component of the 2537 Å resonance line of mercury. By determining the absorbance of this component by mercury vapor, the quantity of the isotope present in the vapor can be determined. The analyses of samples of mercury containing various percentages of Hg-202 agree with values obtained by mass spectrometric methods to within two per cent. The method has the advantage over the mass spectrometer of requiring very much smaller samples. Furthermore, contamination from "hang-up" of previous samples is avoided. Through the use of other isotopic sources it is shown that the method could be extended to the analysis of the remaining isotopes of mercury.

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The Determination of Hg-202 and Other Mercury Isotopes in Samples of
Mercury Vapor by Mercury Resonance Radiation Absorbiometry

The isotopic analysis of samples of mercury by means of the mass spectrometer is complicated by the tendency of the vapor to "hang up" in the inlet system of the instrument. Under such conditions succeeding samples will show contamination due to adsorbed mercury from previous analyses. The situation becomes particularly serious when the quantity of sample available is small.

During the course of an investigation in this laboratory of the mercury-6(3P_1)-photosensitized decomposition of isopropyl chloride, in which an Hg-202 electrodeless discharge tube was used as the source of resonance radiation, it became necessary to determine the atom-per cent Hg-202 in the mercury present in the calomel product of the reaction. A method has been developed for this purpose involving the absorption of resonance radiation, by means of which analyses can be made on microgram quantities of mercury rapidly and with good precision. Furthermore, it will be shown that the method can be easily extended to the determination of other mercury isotopes.

The hyperfine structure of the $\lambda 2537 \text{ \AA}^0$ resonance line of mercury has been shown to consist of five resolvable hyperfine lines. Some of these lines arise from a single even-mass isotope, while others are formed from the superimposition of components from several isotopes. The pertinent data (1) are given in Table 1.

(1) Cojan, J. L. and Lennier, R., Compt. Rend. 235, 1634 (1952)

Table 1

Isotopic Origin and Displacement for the Five Resolvable Hyperfine Components of the $2537 \text{ \AA}$ Resonance Line of Mercury

Displacement of Components from Hg-200 Line m $\text{\AA}$	Contributing Isotopes	Designation of Hyperfine Line Used in this Paper
-24.80	Hg-199, Hg-201	V
- 9.80	Hg-198, Hg-201	W
0.0	Hg-200	X
+11.50	Hg-202	Y
+22.25	Hg-199, Hg-201, Hg-204	Z

It will be noted from the table that the X and Y components arise exclusively from Hg-200 and Hg-202, respectively. Hence if a beam of either of these components is allowed to traverse mercury vapor the fractional absorption will be a function of the number of atoms of the corresponding isotope present in the vapor.

Convenient sources of single hyperfine components have recently become available through the production of highly enriched mercury isotopes. In this investigation a source was used which contains Hg-202 for the generation of the Y component of the resonance line.

Apparatus and Procedure

The optical system used for the absorption measurements is shown schematically in Figure 1. The entire assembly was mounted on a one-meter optical bench. The fused quartz lenses served to confine the beam within the periphery of the absorption cell and focus the transmitted radiation on to the photocell.

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FIGURE 1. OPTICAL SYSTEM FOR THE ABSORPTION MEASUREMENTS.

The construction of electrodeless discharge sources containing single isotopes of mercury has been described elsewhere (2,3). The type

- (2) Meggers, W. F. and Westfall, F. O., Nat. Bur. Standards Research Paper, R.P. 2091, Vol. 44 (1950)
(3) Zelikoff, M., Wyckoff, P. H., Aschenbrand, M., and Loomis, R. S., J. Opt. Soc., 42, 818 (1952)
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used in this work consisted of a quartz tube, 8 mm O.D. and 150 mm in length. The tube contained a small drop of mercury, 98.3 atom per cent in Hg-202, together with a few mm of argon. The discharge was maintained by a Baird 2450 megacycle microwave generator.

The intensity of the Y component transmitted through the absorption cell was measured by a Westinghouse WL 775 tantalum phototube. The photocell was operated at 90 volts, supplied by banks of "B" batteries. Since the photocell responds only in the 2000-3000 Å region, no precautions are necessary in shielding against visible light. A Beckmann Ultrahmeter was used to measure the photocell current. The response was found to be linear in the light intensity for all intensities measured in this investigation.

Since the microwave generator induces marked increases in the noise level in the Ultrahmeter, the entire absorption assembly, including the microwave generator, was enclosed in a large grounded metal box. Under these conditions the Ultrahmeter, which was placed external to the box, showed excellent stability.

In the initial experiments, Aminco, style F, fused quartz absorption cells were used, of path lengths 5.000 and 1.000 cm. The cells were fitted with a side tube and a quartz-to-Pyrex graded seal. In general, the procedure was to evacuate the cell through two U-traps in series with a three-stage oil diffusion pump. With the traps immersed

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in liquid nitrogen, the cell was heated twice to a dull-red heat in order to remove all traces of adsorbed mercury from previous analyses. After the cleaning operation the cell was sealed off from the system. An assembly consisting of the cleaned cell, a fresh U-trap, and the mercury sample contained in a breakseal tube, was then attached via a stopcock to the system.

After evacuation the mercury sample was transferred to the side tube of the cell; whereupon the cell and side tube were sealed off from the system. The cell was attached in a reproducible fashion to a graduated worm-screw clamp on the optical bench, by which means the cell could be conveniently moved in and out of the light beam. The mercury in the side tube was maintained at fixed temperatures by placing suitable slush baths around the side tube. However, the absorption data showed that the concentration of mercury vapor in the light path fluctuated with changes in laboratory temperature. The difficulty was obviated by using a style F cell with a 0.1003 cm path length. The effective temperature range for this cell was 12-40°C. Hence the entire cell and side tube could be immersed in a water thermostat, controlled to 0.1°C. Plates of Vycor 7910 glass mounted in opposing faces of the thermostat box served as entrance and exit windows for the light beam. The Vycor plates also removed any 1849 Å radiation present in the incident beam. The photocell reading (R_0) for the mercury-free cell was obtained with the mercury frozen with liquid nitrogen in the side tube. The freeze-out operation was accomplished by pouring the refrigerant over a sheath of glass wool which had been wrapped around the sidearm. For this measurement the water level in the thermostat was reduced so that the side arm protruded into air, while the remainder of the cell was immersed. The R_0 reading was taken after each transmittance measurement on a mercury sample.

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The fractional transmittance was taken as the ratio of the Ultrahrometer reading (R) with the cell filled with mercury vapor at a given thermostat temperature to that for the empty cell (R_0). Since resonance absorption only occurs in the overlap of the emission and the absorption line contours, the measured transmittance was strongly influenced by both the half-width and the shape of the emission line, which in turn depended upon the orientation and excitation conditions of the source. With the lamp mounted head-on, parallel to the optical axis of the apparatus, a good point source was obtained. However, the absorption was slight owing to self-reversal of the emission line. This condition was caused by the fact that the discharge was concentrated at the center of the lamp. Reversal would therefore arise through absorption by the cooler mercury between the center and the exit end of the lamp. A satisfactory unreversed line was obtained by taking the radiation from the side of the lamp with the long axis of the lamp oriented perpendicular to the optical axis of the apparatus. The arrangement is shown in Figure 1.

Another factor which markedly affected the width and shape of the emission line was the method of cooling the lamp. The lower the lamp temperature the better the superimposition of emission line on absorption line, and the smaller the danger of overlap of the emission line on the absorption lines of adjacent hyperfine components. Hence the lamp was operated at as low a temperature as was compatible with lamp stability. Cooling was achieved by surrounding the lamp with a quartz jacket, and allowing a fast stream of water to flow over the lamp, which was supported by a copper coil as shown in Figure 1. Since the microwave field is strongly absorbed by water, it was necessary to keep the sheath of cooling water as thin as possible in order to maintain a stable discharge in the lamp. The temperature of the lamp was made constant by circulating the

cooling water through a thermostat which was maintained at 25°C. In Table 2 the effects are shown of various lamp conditions on the transmittance readings.

Table 2

The Influence of Lamp Conditions on the Transmittance Values for a Constant Mercury Pressure in the Absorption Cell

Series*	Lamp Conditions	Fractional Transmittance (R/R_0)	Per Cent Absorbance
A	Well-cooled lamp in vertical position	0.357	64.3
A	Well-cooled lamp, mounted head-on	0.510	49.0
A	Hot lamp, in vertical position	0.470	53.0
B	Lamp vertical, cooling water at 25°C	0.561	43.9
B	Lamp vertical, cooling water at 35°C	0.640	36.0

* Series A and B are not comparable since the samples of mercury in the absorption cell were at different temperatures.

It is apparent from Table 2 that meaningful transmittance data can only be obtained when lamp conditions are rigorously controlled. Finally the influences of the output of the microwave director and the distance away from the microwave director on the lamp characteristics were studied. It was found that the shape of the emission line was relatively insensitive to the aforementioned variables. However, great care was taken to maintain a fixed orientation of the lamp with respect to the microwave director.

Results and Discussion

In order to calculate the mercury vapor pressure in the absorption cell for various bath temperatures, an equation derived from data summarized by Busey and Giaque (4) was used:

 (4) Busey, R. H. and Giaque, W. F., J. Am. Chem. Soc., 75, 806 (1953)

$$\log_{10} P(\text{atmos.}) = \frac{-3.185 \times 10^3}{T} + 5.109$$

The theory of the absorption of mercury resonance radiation by mercury vapor has been thoroughly discussed by Mitchell and Zemansky (5).

 (5) Mitchell, A. C. G. and Zemansky, M. W. "Resonance Radiation and Excited Atoms", Cambridge (1934)

Only the factors pertinent to the analytical technique will be mentioned here.

If a collimated beam of a single hyperfine component of half-width, $\Delta \nu_E \text{ sec}^{-1}$, is allowed to traverse 1 cm of mercury vapor of concentration $N \text{ atoms/cm}^3$, and with an absorption line half-width of $\Delta \nu_A \text{ sec}^{-1}$, the fractional absorption, A_α , of the beam can be calculated from the series

$$A_\alpha = \frac{(k_0 l)}{\sqrt{1+\alpha^2}} - \frac{(k_0 l)^2}{2! \sqrt{1+2\alpha^2}} + \dots + (-1)^{(n-1)} \frac{(k_0 l)^n}{n! \sqrt{1+n\alpha^2}} + \dots$$

where k_0 is the ideal maximum absorption coefficient in cm^{-1} and

$$\alpha = \Delta \nu_E / \Delta \nu_A.$$

For a given source the relation between the observed fractional absorbance, A , and the concentration, N , of the absorbing species can be evaluated once α , the ratio of the half-widths of the emission to the absorption lines, has been determined. This is true since k_0 is proportional to N .

The method developed by Zemansky (6) was employed to determine the value of α for the present system. To this end the observed absorbance,

(6) Zemansky, M. W., Phys. Rev. 36, 219 (1930)

A, was measured over a range of values of N, using a sample of natural mercury in the cell. Here N represents the concentration in atoms/cm³ of the Hg-202 present in the mercury. From the series expansion above, a family of curves was constructed of $A \alpha$ vs. $k_0 l$ for various values of α . The value of α applicable for our system was found by choosing the theoretical curve which yielded a linear relation between N and k_0 . For our system α was thereby found to have a value of 1.7.

The magnitude of α is critical since it determines to what extent the emission line overlaps the contours of the hyperfine absorption lines adjacent to the principal absorption line. Since pressures were low in the absorption cell, the absorption line for the Hg-202 isotope can be regarded as a pure Doppler line. Hence its half-width, $\Delta \nu_A$ will be given by the equation

$$\Delta \nu_A = \frac{2 \sqrt{2R \ln 2}}{c} \cdot \nu_0 \cdot \sqrt{\frac{T}{M}}$$

where C = velocity of light in cm/sec; R = gas constant in ergs/mole/degree; ν_0 = frequency in sec⁻¹ at the center of the absorption line; T = absolute temperature and M = gram-molecular weight of the absorbing species.

For our system $\Delta \nu_A$ was calculated to be 1.02×10^9 sec⁻¹. Hence $\Delta \nu_E = \alpha \Delta \nu_A = 1.7 \times 10^9$ sec⁻¹. From Table 1 it can be seen that the Z component is the nearest to the Y component employed in this study. The separation is 10.75 mÅ or 5.0×10^9 sec⁻¹. It can therefore

be seen that no overlap of the emission line on adjacent components can occur. The observed absorption must consequently arise exclusively from the Hg-202 atoms present in the cell.

Once the apparatus had been calibrated, using the 0.1003 cm absorption cell, analyses of a number of samples were made by determining the absorbance for each sample over the range from 12-40°C in cell temperature. Each sample was also analyzed with a Model-21-109 Consolidated mass spectrometer. The data are summarized in Table 3.

Table 3

A Comparison of Hg-202 Analyses of Various Mercury Samples by the Present Resonance Absorption Method and by the Mass Spectrometer

Sample	Absorption Method Atom-Per Cent of Hg-202	Mass Spectrometer Atom-Per Cent of Hg-202	Per Cent Deviation
Natural mercury	29.2	29.6	1.4
AEC-enriched sample	93.3	95.1	1.9
2-88B	35.2	36.4	3.4
2-94	40.8	35.8	14.0
2-97	37.8	37.0	2.2
4-29A	31.0	30.5	1.6

Repeated trials on the same sample by the absorption method showed maximum deviations of one per cent. Larger variations were observed with the mass spectrometer. From Table 2 it can be seen that, with the exception of sample 2-94, agreement between the two methods is within two per cent on the average. Sample 2-94 was checked several times by the absorption method and results within one per cent were obtained. It is suspected that the mass spectrometer value for this sample is low through

contamination from a sample of natural mercury which had been run immediately before the reported analysis.

A major advantage of the absorption technique over the mass spectrometer is the size of sample required. Thus only a few micrograms of mercury are required for the absorption method. Samples at least one thousand times larger are needed for the mass spectrometer.

It is apparent that the absorption method could be fairly straightforwardly extended to the determination of certain other isotopes in mercury. The total number of atoms/cm³, N_T , in a given mercury sample is known from the vapor pressure. Neglecting the small fraction of Hg-196 normally present,

$$N_T = N_{198} + N_{199} + N_{200} + N_{201} + N_{202} + N_{204}.$$

Through the use of Hg-200, Hg-202 and Hg-204 sources, N_{200} , N_{202} , and $(N_{199} + N_{201} + N_{204})$ may be directly determined. By difference N_{198} may then be obtained. Through the use of an Hg-198 source the sum $(N_{198} + N_{201})$ could be evaluated, and thus N_{201} could be found by difference. Hence at least four of the six isotopes in mercury and the sum of the other two should be capable of measurement by the present method.

Acknowledgment

The authors would like to express their deep appreciation to Dr. C. C. McDonald of this laboratory for helpful advice and discussion. A very special measure of thanks is also due Dr. W. F. Meggers and his staff at the Spectroscopy Section of the National Bureau of Standards for their kindness in fabricating the Hg-202 sources used in this investigation. The assistance of the AEC through its support of this work is most gratefully acknowledged.

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