Mercury Monitor for Ambient Air

Abstract. *An isotope-shift, Zeeman-effect atomic absorption spectrometer has been demonstrated to have sufficient sensitivity to continuously monitor the total mercury content of ambient air. At present, the minimum total mercury concentration detectable with this device is 0.2 microgram per cubic meter of air—one fifth of the proposed federal guideline. This is the first technique which responds to both mercury vapor and mercury in particulates available for continuous monitoring at this concentration.*

The proposed federal guideline for the maximum allowable mercury concentration in air to which the general public may be exposed is 1 μg/m^3 (*1*). At present, convenient techniques do not exist to continuously monitor the total mercury content of air at this concentration. We report a series of measurements which demonstrate that the refined version of the isotope-shift, Zeeman-effect atomic absorption (IZAA) mercury detector described here has adequate sensitivity for such continuous monitoring.

Recently we reported the development of a new type of atomic absorption spectrometer which makes possible the measurement of the mercury content of a solid or liquid sample in less than a minute without previous chemical separation of the mercury from the host material (*2*). In this technique, the sample is thermally decomposed in a furnace maintained at a temperature near 1000°C. The decomposition products are then swept into a heated absorption tube by a stream of carrier gas. Here they are probed with a light beam that has two constituents; one has a wavelength centered on the absorption profile of natural mercury in air, and the other is slightly displaced (less than 1 cm^{-1}) from the absorption line. The absorption of the centered constituent is due to mercury vapor as well as to nonmercury decomposition products —particulates (smoke) and any thermally stable molecular species present; the absorption of the displaced constituent is due only to the nonmercury background. In the vicinity of the 2537-Å line of mercury, this background absorption does not change significantly over 1 cm^{-1}. Consequently, by taking the difference between the absorption of the two constituents, one measures the absorption due to mercury alone. This background cancellation results in strong discrimination against interferences.

The heart of the technique lies in the method by which the probe and the reference constituents are generated, and the mode by which these are distinguished from each other; we report here major changes that we have made in the previously reported technique. In our present apparatus (Fig. 1) both constituents are supplied by a single ^{204}Hg electrodeless-discharge lamp operated in a 15-kgauss magnetic field. The isotope shift and the Zeeman effect combine to give probe and reference constituents with appropriate wavelengths which are linearly polarized perpendicular to each other (*3*). These constituents are alternately allowed to pass through the absorption tube; to switch from one to the other, we use a current-controlled, variable phase–retardation plate followed by a linear polarizer (*4*).

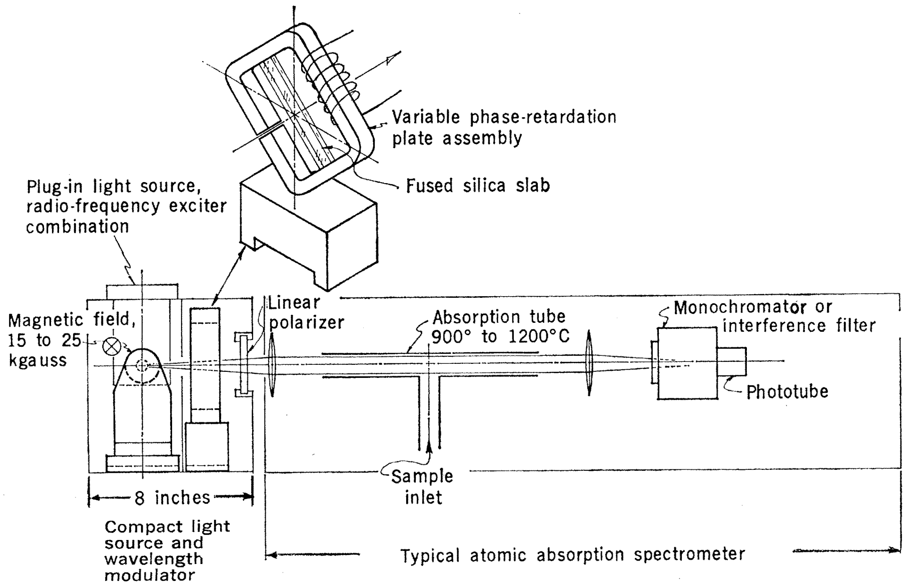

Fig. 1. Schematic diagram of the IZAA spectrometer as used in the present experiment.

This variable phase–retardation plate consists of a plate of fused quartz held in a magnetic clamp. When no current is flowing through the magnet coil, the quartz leaves the polarization of the light passing through it unaltered. The linear polarizer then permits only the probe constituent to reach the absorption tube. In contrast, when a properly chosen current actuates the magnetic clamp, the quartz becomes birefringent and acts as a half-wave plate. It rotates the polarization of both constituents by 90°, so that now only the reference constituent passes the linear polarizer.

After traversing the absorption tube and an interference filter, both constituents alternately fall upon a photodetector. In the absence of atomic mercury in the absorption tube, and with a nonmercury background present or not, the output of the photodetector is independent of whichever constituent is incident upon it (*5*). In the presence of mercury, the output is modulated by the switching between constituents. In the present device, the switching frequency is 250 hertz; the a-c signal from the photodetector at this frequency is conveniently extracted with a lock-in amplifier. The amplitude of this signal serves as a measure of the quantity of mercury in the absorption tube.

The lower limit of detection (LLD) of the instrument was determined with the use of a cylindrical cell that was attached to a sidearm. The cell contained a small amount of liquid mercury and was filled to a pressure of about 1 atm with argon. A diaphragm was placed in the light path of the instrument near the point at which the cell was positioned so that the volume of the cell that was intersected by the light beam could be defined. The sidearm of the cell was placed in an ice bath so that the vapor pressure of the mercury would be defined. Knowing the volume and the vapor pressure allowed the weight of mercury responsible for an observed meter deflection to be calculated. By next determining the noise level, the LLD could be calculated (the LLD is equal to twice the noise level).

This procedure turned out to be more difficult than anticipated. Problems arose because long times were required for the complete mixing of the mercury vapor and the argon gas in the absorption cell. The time required was reduced by placing the sidearm in a bath of liquid nitrogen which liquefied the argon. The cell was next positioned such that the cylindrical portion was in a small furnace and the sidearm was in an ice bath. This arrangement favored the formation of convection currents. After this procedure the cell was placed in the instrument, but no readings were taken until a meter displacement that did not vary with time was obtained; the time required was between 1 and 2 hours.

In order to discover if serious mercury losses occur in a typical sampling system, an independent (but less precise) method was used to determine the LLD. Approximately 1 ml of mercury was placed in a septum-covered test tube which was maintained at 0°C by an ice bath. We withdrew air and mercury vapor from the test tube with a syringe which penetrated the septum. A diaphragm-type sampling pump was used to force air through the furnace. The sampling line was fitted with two Y tubes, one ahead of the pump and one behind it. Each Y tube was fitted with a septum. By injecting 100 pg of mercury vapor ahead of and behind the pump, it was determined that 30 percent of the sample was lost in the sampling system. The airstream flowed from the pump into the expansion chamber of the furnace (*6*); in this chamber, the mercury vapor mixed with air continuously flowing at 6.8 ml/sec. The calculation of the mercury concentration present in each measurement is based upon the assumption of complete mixing in this chamber.

This assumption was checked in two ways. First, a glass chamber was made of the same shape as the expansion chamber. With the same flow of carrier gas through this chamber as is normally used, we injected a sample of smoke from a syringe in the same way as the mercury vapor sample had been introduced into the IZAA spectrometer. Visual observation of the smoke behavior indicated that the mixing was quite good. Second, we calculated the shape of the expected output signal from the lock-in amplifier on the assumption of complete mixing and got reasonable agreement with the observed shape (*7*). Calculations of LLD by this method gave results that were within a factor of 2 of the value obtained by the absorption cell method. This difference is believed to be due to the approximations made in the equation used to calculate the time variation of mercury in the absorption region.

Figure 2 presents the results of one series of measurements made at low concentration. In Fig. 2a, the peak concentrations of mercury for curves 1, 2, and 3 are, respectively, 11, 1.1, and 0.55 μg/m^3. In Fig. 2b, we plot peak height versus the volume of mercury vapor injected into the furnace; this curve illustrates that, over the concentration range of 0 to 11 μg/m^3, the response of the instrument is linear with concentration. Measurements were extended to a calculated concentration of 66 μg/m^3, with no apparent deviation from linearity. Peak area versus concentration was also plotted with essentially identical results. From these measurements we estimate that the minimum detectable concentration of mercury for this instrument, used in the mode described above, is at least 0.2 μg/m^3. In a practical continuous-flow system, an improvement in sensitivity of an order of magnitude or more is to be expected from the increase in integration time alone.

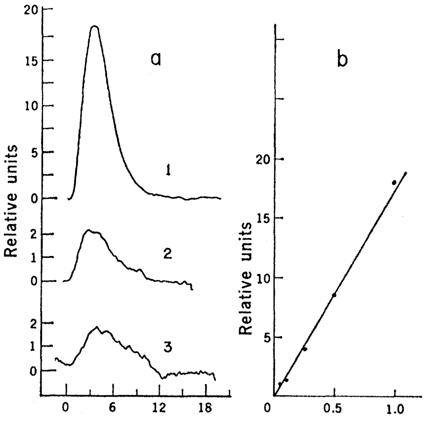

Fig. 2. (a) Curves 1, 2, and 3 are plots of the lock-in amplifier output as a function of time for pulses of gas containing 11, 1.1, and 0.55 μg of mercury per cubic meter of air admitted at time $t = 0$. (b) The pulses were provided by injecting known volumes of mercury vapor at standard temperature and pressure into the instrument. The plot gives peak height as a function of the volume of injected mercury vapor. The mercury concentration range is 0 to 11 μg/m^3.

Mercury may be present in the atmosphere in a variety of forms (atomic vapor, particulates, organometallic vapor). Earlier work (*8*) has demonstrated that the signal obtained from this instrument is independent of the form of mercury entering the furnace. For this reason the total mercury content of the airstream will be obtained.

The changes in the IZAA technique which made these measurements possible increased the sensitivity by a factor of 100, greatly improved the background cancellation, and increased the stability. The performance of the IZAA spectrometer as reflected here marks its emergence from the status of laboratory curiosity into the category of a widely useful tool for routine monitoring (*9*).

T. HADEISHI, D. A. CHURCH
R. D. MCLAUGHLIN, B. D. ZAK
M. NAKAMURA, B. CHANG
Lawrence Berkeley Laboratory,
University of California,
Berkeley 94720

References and Notes

1. "Background information—Proposed national emission standards for hazardous air pollutants: asbestos, beryllium, mercury" (Environmental Protection Agency Publication APTD 0753, Air Pollution Technical Information Center, Research Triangle Park, N.C., Dec. 1971).
2. T. Hadeishi and R. D. McLaughlin, *Science* **174**, 404 (1971); T. Hadeishi, *Appl. Phys. Lett.* **21**, 438 (1972).
3. A more detailed description of the apparatus is available in *Lawrence Berkeley Lab. Rep. 1593* (1973); address requests for copies to R.D.McL.
4. T. Hadeishi *et al.*, in preparation.
5. In order to obtain this condition, the intensities of the probe and the reference constituents incident upon the absorption tube must be equal; see *Lawrence Berkeley Lab. Rep. 1593* (1973).
6. The expansion chamber is schematically indicated by the leg of the "T" in Fig. 1.
7. The expression we derive for the quantity of mercury, $N_a(t)$, in the absorption tube as a function of time t is:

$$N_a(t) = \frac{N_0 V_a}{(V_0 - V_a)}\left[\exp\left(-\frac{Rt}{V_0}\right) - \exp\left(-\frac{Rt}{V_a}\right)\right]$$

where N_0 is the quantity of mercury injected, V_0 is the volume of the expansion chamber, V_a is the volume of the absorption tube, and R is the carrier gas flow rate.
8. D. A. Church, T. Hadeishi, L. Leong, R. D. McLaughlin, B. D. Zak, *Anal. Chem.* **46**, 1352 (1974).
9. In addition to a portable, modular version of the IZAA mercury detector, we have constructed similar instruments for cadmium and lead. The IZAA technique is applicable to most of the elements for which a suitable lamp can be made.
10. We thank D. MacDonald for his mechanical design work, W. Berlund for his construction of light sources, and D. Nelson and C. Dols for help in the initial development of the current-controlled variable phase-retardation plate. Work supported by the RANN program of the National Science Foundation and by the U.S. Atomic Energy Commission.

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