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# HYPERFINE-ZEEMAN-EFFECT ATOMIC ABSORPTION SPECTROMETER FOR MERCURY

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## ABSTRACT

A new type of atomic absorption spectrometer — one that detects trace mercury in host material, based on hyperfine-structure lines in a magnetic field — was developed and tested on various substances. This device can detect trace mercury to about 0.04 ppm (40 ppb) in about 1 minute. No chemical separation from the host material is necessary.



A problem of great importance today is the detection of mercury in food, especially in fish such as tuna and swordfish. Unfortunately, so far as we know, no device available can make a rapid analysis of mercury to about 0.1 ppm in about 1 minute without first separating the mercury from the host material. Because of the urgent need for the detection of mercury, we have converted to this purpose a mercury optical-pumping nuclear magnetic resonance magnetometer (1) which we had constructed earlier to measure magnetic fields. We were motivated to utilize this technique because we are able to observe routinely in our magnetometer a magnetic resonance signal whose equivalent density is about $10^{10}$ to $10^{11}$ atoms per $cm^3$. This corresponds to about $10^{-12}$ g of mercury per $cm^3$. Because of the intrinsic sensitivity of this apparatus and because considerable work had been done to construct a stable, intense, sharp mercury lamp and associated electronics, we felt that converting the magnetometer to a mercury detector would be of interest.

Our objective was to develop an instrument that can be operated by completely inexperienced personnel (such as fishermen), which has high accuracy in mercury detection to at least 0.04 ppm (40 ppb), which is very rapid in analysis without any chemical separation from the host material, and which is inexpensive. We believe that the prototype instrument we developed satisfies the above aims, although the unit in its present form is not quite portable because we used readily available materials rather than engineering a commercial-type unit.

For the sake of simplicity in illustrating the principle of operation of this device, we describe first an ideal case and then an alternative way to approach this ideal condition, which is more difficult to

achieve in practice. Let us consider an even-isotope mercury lamp placed in a high magnetic field (about 20 to 30 kG). The resonance radiation of $\lambda = 2537$ Å, corresponding to the $^3P_1 \rightarrow {}^1S_0$ transitions, is split into three components: $\sigma^+$, $\pi$, and $\sigma^-$. The light emitted in the direction normal to the magnetic field consists of three Zeeman components whose frequencies are given by

$$\nu(\sigma^+) = \nu_0 + \delta\nu,$$
$$\nu(\pi) = \nu_0,$$
$$\nu(\sigma^-) = \nu_0 - \delta\nu, \qquad (1)$$

where $\delta\nu$ is the shift in the frequency due to the Zeeman effect, given by

$$\delta\nu = \left(\frac{g_J\beta}{h}\right) H, \text{ in the usual notation.}$$

The absorption profile of mercury in air is pressure-broadened (2) so that the absorption width is much wider than the Doppler width. However, $\delta\nu$ in Eq. (1) is linear in a magnetic field H, so that, at least in principle, if the magnetic field is increased, two of the Zeeman components, $\sigma^+$ and $\sigma^-$, will lie outside the absorption profile and the $\pi$ component will lie inside the absorption profile. At atmospheric pressure the Doppler effect is negligible, and the absorption broadening is entirely due to the pressure effect. On the other hand, the line profile of the resonance radiation is that of the Doppler width of the low-pressure electrodeless mercury lamp. We made this lamp with an effective lamp temperature of about 300 °K. The shape of the 2537-Å light profile was checked with a Fabry-Perot interferometer as well as by Bitter's magneto-optical scanning method (3).

In order to determine the trace mercury from the host material with no initial chemical separation, the host material is heated in the absorption furnace to decompose its mercury compounds to mercury



metal. In addition to mercury, complex chemical byproducts also fill the furnace, whether we heat the host material simply in air or in an oxygen-rich atmosphere. These nonmercury components either scatter or absorb the 2537-Å radiation. This phenomenon has hitherto made the determination of trace mercury to even 10 ppm impossible without prior extraction of metallic mercury from the host material. However, the absorption or scattering by nonmercury vapors in general varies very slowly in the vicinity of 2537 Å, so we can assume that the amount of absorption or scattering by nonmercury vapor is the same for the $\sigma^+$, $\pi$, and $\sigma^-$ lines. Thus, if we construct a device that detects the difference of absorption between the total monitoring light $I_S = I(\sigma^+) + I(\sigma^-) + I(\pi)$ and the reference light $I_R = I(\sigma^+) + I(\sigma^-)$, we get the effect of absorption by mercury <u>only</u>, provided the absorption by nonmercury vapor is not close to 100%. Figure 1 is a block diagram of such a device. Because of the mercury cell (Hg in 1 atmosphere of Ar or $N_2$) in front of the photodetector #2, the intensity of the light $I_R$ impinging on this detector is entirely due to the $\sigma^+$ and $\sigma^-$ components, which we denote as

$$I_R = I(\sigma^+) + I(\sigma^-) = I_{out},$$

whereas the intensity of the light $I_S$ impinging on the photodetector #1 contains all these components, given by

$$I_S = I(\sigma^+) + I(\sigma^-) + I(\pi) = I_{out} + I_{in}.$$

Here S stands for the intensity of the light containing the signal due to mercury and R stands for the nonmercury reference; $I_{out}$ for the intensity of the Zeeman components lying outside the absorption profile and $I_{in}$ for those lying within. The photoelectric current, and hence the output voltages of photomultipliers #1 and #2, is proportional to $I_S$ and $I_R$. Thus, the output voltages can be represented as

$$V_S = k_1 I_S \quad \text{and} \quad V_R = k_2 I_R,$$

where $k_1$ and $k_2$ account for the quantum efficiency of the photodetectors, the gain, the geometrical factor, etc. In the absence of a sample containing mercury in the absorption cell, we can set $V_{out} = V^0_{out} = V_S - V_R = 0$, either by adjusting the light intensity of $I_S$ and $I_R$, or by means of the amplifier gains $A_1$ and $A_2$ (see Fig. 2). Thus we have

$$V_{out} = V^0_{out} = k_1 I_S - k_2 I_R = 0, \tag{2}$$

so that

$$k_1 = \frac{k_2 I_R}{I_S} = \frac{k_2 I_{out}}{I_{out} + I_{in}}. \tag{3}$$

If we now introduce a sample containing mercury in the host material into the absorption cell (furnace), the transmitted light intensities for $I_S$ and $I_R$ are given by

$$I_S = I_{in}(1 - \alpha_{Hg} - \alpha_n) + I_{out}(1 - \alpha_n),$$

$$I_R = I_{out}(1 - \alpha_n), \tag{4}$$

where $\alpha_{Hg}$ is absorption by mercury and $\alpha_n$ is absorption or scattering by nonmercury elements (n stands for nonmercury materials, or smoke). Therefore we get

$$V_{out} = k_1 I_S - k_2 I_R = -k_1 \left(\frac{I_{in}}{I_{in} + I_{out}}\right) I_{in}\alpha_{Hg}$$

$$= -k_2 \left(\frac{I_{in}}{I_{in} + I_{out}}\right) I_{out}\alpha_{Hg}. \tag{5}$$

Thus, $V_{out}$ is <u>proportional</u> to the mercury absorption, and the effect of nonmercury is completely eliminated.

In the actual practice of detecting mercury in the host material, it is not convenient to use the normal Zeeman effect described above:



the width of the absorption profile is so large, because of pressure broadening, that we would need an unreasonably large magnetic field to get $I_{out}$ sufficiently far away from the absorption profile (more than 20 kG). This would add the cost and weight of a relatively large magnet to the instrument. To overcome this difficulty, we used a $^{199}$Hg source, since the hyperfine structures of $^{199}$Hg in the $^3P_1$ state lie at the two extreme ends of the isotope distribution of natural mercury.

Figure 2 shows the Zeeman effect of $^{199}$Hg along with the energy levels of the natural mercury isotopes. From Fig. 2 it is evident that we gain about 12 GHz in Zeeman separation over the normal Zeeman effect we discussed previously [$^{199}\Delta\nu(^3P_1) = 22{,}128.650$ MHz] (4). However, the pressure-broadened profile of natural Hg (about 10% $^{198}$Hg, 28% $^{200}$Hg, 13% $^{201}$Hg, and 20% $^{202}$Hg) overlaps these two hyperfine levels in a zero magnetic field. So we need a further shift in the hyperfine lines. This can be accomplished by the Zeeman effect.

About a 10-kG magnetic field can shift the hyperfine Zeeman levels $|F = 3/2, m_F = 3/2\rangle$, $|F = 3/2, m_F = 1/2\rangle$, and $|F = 1/2, m_F = -1/2\rangle$ of $^{199}$Hg sufficiently far away that the optical Zeeman components originating from these three levels can be used as $I_{out}$, described earlier. The remaining Zeeman lines originating from $|F = 3/2, m_F = -1/2\rangle$, $|F = 3/2, m_F = -3/2\rangle$, and $|F = 1/2, m_F = 1/2\rangle$ play the role of $I_{in}$. Thus we were able to use a light-weight permanent magnet and still obtain sufficient shifts in the hfs Zeeman lines to obtain an $I_{out}$ reference signal for elimination of the nonmercury effect.

The performance of the instrument we constructed was tested against our standard (which we made by mixing HgI into carbon, and HgO into carbon and starch). In addition, we ignited various materials

materials containing no mercury in the furnace to ascertain that $V_{out}$ remained zero in the absence of mercury in spite of smoke, steam, etc. We also used our standard to determine $k_1$ and $k_2$. We calibrated the instrument against the standards, and tested our apparatus for mercury on tuna supplied and analyzed by the National Canners Association (by standard chemical analysis); we obtained good agreement with our standard. We placed varying amounts of tuna containing 0.49 ppm and 0.24 ppm of Hg in the furnace and made a plot of ng of Hg vs. area under the Hg absorption signal. All samples were within 12% of the average over the range from 5 to 35 ng. After these tests, we measured mercury concentrations in various materials such as wall paints, papers, and meats. Figure 3 shows a typical signal $V_{out}$ along with $V_R$ and $V_S$.

This technique is not limited to the detection of mercury; we believe it can be extended to almost every element in which the atomic absorption technique is applicable. The block diagram (Fig. 1) illustrates only the principle behind the instrument. In the actual instrument we used an automatic heating furnace, a phase-sensitive detector to eliminate extraneous light interference, and a digital integrator. The instrument performance would be improved by the use of an automatic light-intensity stabilizer and an automatic gain control against the attenuation of $I_R$ and $I_S$ due to $\alpha_n$.

No great effort was made to increase the capability of this instrument to the limit. With improved electronics it should be possible to reach $10^{-11}$ g/cc of Hg atom determination. This corresponds to about 0.1 ppb sensitivity for a 10-mg sample.



## References and Note


1. B. Cagnac, Ann. Phys. 6, 467 (1961).
2. See, for example, A. C. E. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms (Cambridge University Press, London and New York, 1961).
3. F. Bitter, H. Plotkin, B. Richter, A. Teriotdale, and J. E. R. Young, Phys. Rev. 91, 421 (1953).
4. F. Bitter, Appl. Opt. 1, 1 (1962).



5. We acknowledge valuable assistance and advice from Michiyuki Nakamura regarding electronics, Maynard Michel for discussion of the chemical processes that may take place in the furnace, Wilton Berlund for glassblowing, and Dick Escobales for furnace design.

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## Figure Legends

Fig. 1. Block diagram illustrating the principle of operation of the device.

Fig. 2. Energy levels of the $6^3P_1$ states of the natural mercury isotopes and the Zeeman pattern of the $^{199}Hg$ states F = 3/2 and F = 1/2. Superimposed on the figure is the pressure-broadened profile of the $6^3P_1$ state of natural Hg in zero magnetic field.

Fig. 3. Recorder tracings of $V_S$, $V_R$ and amplified Hg signal, $-G \times V_{out}$ for tuna meat, where -G is the gain of the amplifier with integration time constant of 0.1 sec. The large drop in $V_S$ and $V_R$ is due to the smoke effect. The temperature indicated is the temperature of the furnace; the temperature of the sample is lower by about 50 to 100 °C.



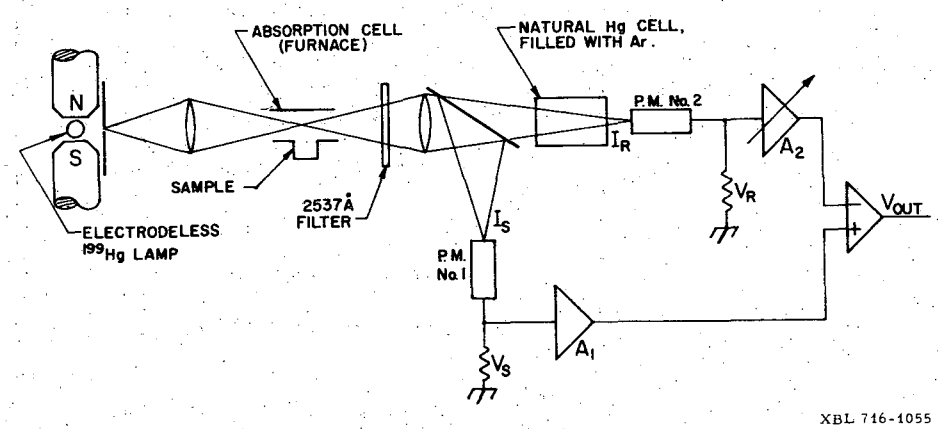


Fig. 1

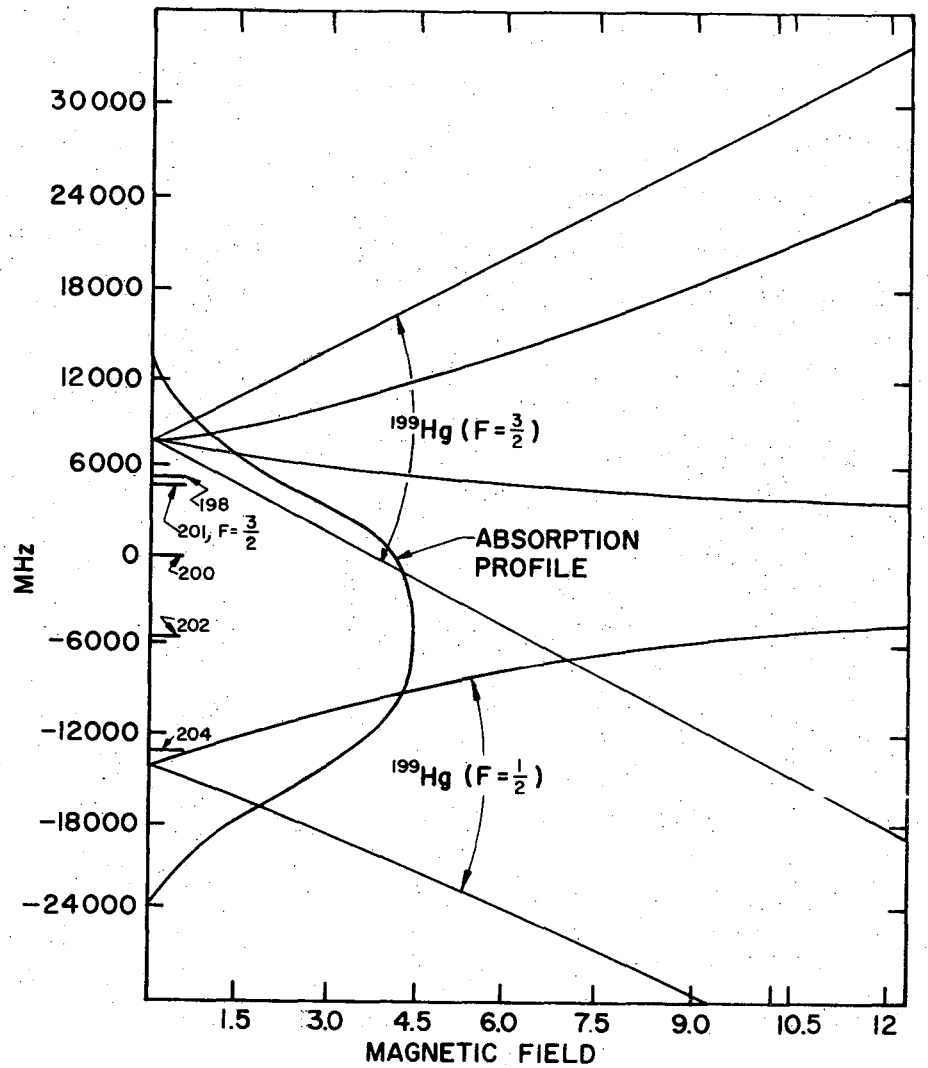


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Fig. 2



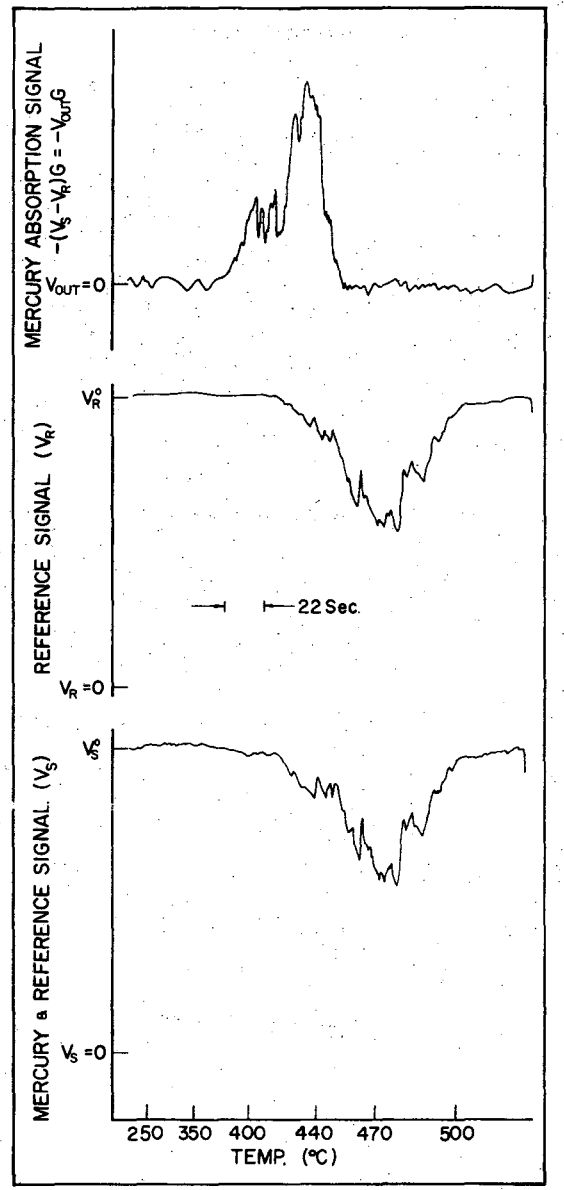


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Fig. 3

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