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Isotope-Shift Zeeman Effect for Trace-Element Detection:
An Application of Atomic Physics to Environmental Problems *

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ABSTRACT

Bitter's magnetic scanning method was applied to the detection of trace amounts of mercury using the Zeeman effect of an isotope-shifted ^{198}Hg line. This new technique for trace element detection makes it possible to detect Hg in the part-per-billion range directly from a host material in a few seconds.

Because of the importance in environmental studies of detecting trace elements, an effort was made at LBL to apply the techniques of atomic physics to problems in environmental research.

The most serious trace element contaminants endangering human health are mercury, arsenic, lead, and cadmium. Unfortunately, no technique seems available for the rapid detection of these elements in the ppb (part-per-billion) range. At present the techniques widely used for trace-element detection are (1) wet chemistry, (2) conventional atomic absorption and fluorescence, (3) x-ray fluorescence, and (4) neutron activation. These techniques are extremely time-consuming, and the reliability of the results of the trace-element determination is strongly dependent on the capabilities of the personnel performing the test.

Since the elements cited above can be easily vaporized by heating, regardless of the original form of the organic compounds, their vapors can be detected most efficiently by optical absorption. The optical absorption cross section is $\sim \pi \lambda^2$ ($\sim 10^{-10} \text{ cm}^2$). However, in ordinary practice, these elements cannot be detected by such a technique without chemical separation from the host material because the complex molecules and particles also vaporize, and interfere with the determination. These molecules either absorb or scatter the resonance radiations that are to be used to detect the trace elements of interest.

We have decided to monitor the atomic vapor and the complex molecular vapors separately by generating two close-lying optical lines ($\sim 1 \text{ cm}^{-1}$ apart): one to monitor the atomic and molecular vapor,

and the other the molecular vapor alone. The difference of optical absorption of these two close-lying optical lines is proportional to the amount of atomic vapor, provided an appropriate means of normalization is made against the attenuation of the light by the molecular vapors. To generate two close-lying optical lines in mercury, we used the Zeeman effect in an even isotope. The absorption peak of naturally-occurring mercury in the atmosphere is shifted to the lower side by the Lorentz effect.¹ Because of the Lorentz shift and broadening, the Zeeman effect was used to bring the σ^- component to the top of the absorption peak and the σ^+ component as far away as possible from the absorption peak. Such a condition can be easily satisfied for almost every element.

This method was originally used by Francis Bitter² to measure the hyperfine structure and isotope shift of naturally-occurring mercury. In Bitter's experiment the mercury vapor was in an evacuated cell, so that there was neither interference from the molecular vapor nor the effect of Lorentz broadening. The determination of mercury from host material (tuna meat, for instance) without chemical separation of the mercury prior to the detection is a more difficult.

Although we could have chosen any one of the elements mentioned at the beginning of this paper, we decided to test the idea on mercury, since mercury seems to be causing the most serious problems. Figure 1 shows the Zeeman-shifted line profile of σ^+ and σ^- of ^{198}Hg in 7 kG; it is superimposed on an absorption profile of naturally-occurring mercury in 1 atmosphere (STP) of N_2 measured by the magnetic

scanning technique developed by Bitter² (using σ^+ and σ^- components of ^{204}Hg). Lorentz broadening and shifting is clearly evident. At 7 kG magnetic field, the σ^- component of ^{198}Hg lies on the top of the absorption peak and the σ^+ component lies considerably away from the peak. Utilizing these properties, the experimental arrangement shown in Fig. 2 can distinguish the two absorptions. By rotating the quarter-wave plate for the 2537-Å line (6^3P_1 to 6^1S_0 intercombination line) the σ^+ and σ^- components are detected alternately by the photomultiplier tube. The intensities $I(\sigma^+)$ and $I(\sigma^-)$ in the absence of Hg in the absorption cell are identical. Thus the photoelectric current (hence the voltage) $V_{\text{out}} = I(\sigma^-) - I(\sigma^+) \equiv 0$. In the presence of absorbing vapor (Hg + complex molecules + smoke):

$$\begin{aligned} V_{\text{out}} &= I(\sigma^-) e^{-\ell \int (k_v^- + k_s) dv} - I(\sigma^+) e^{-\ell \int (k_v^+ + k_s) dv} \\ &= \frac{I}{2} \left[e^{-\ell \int k_v^- dv} - e^{-\ell \int k_v^+ dv} \right] e^{-\ell \int k_s dv}, \end{aligned}$$

since $I = I(\sigma^+) + I(\sigma^-)$ and $I(\sigma^+) = I(\sigma^-)$, where k_v^- and k_v^+ are the respective coefficients of absorption for the σ^- and σ^+ components, and k_s is the broadband absorption coefficient of the non-Hg components — which is very likely the same for $I(\sigma^+)$ and $I(\sigma^-)$. By means of a voltage-controlled amplifier, remotely controlled by a smoke monitor, we can in effect keep $e^{-\ell \int k_s dv} = \text{constant}$, regardless of the amount of smoke, up to about 90% of attenuation of the light by non-mercury absorption or scattering.

Hence, for small absorption,

$$V_{\text{out}} = V_{\text{sig}} \propto -\ell \left[\int k_{\nu}^{-} d\nu - \int k_{\nu}^{+} d\nu \right] \propto -\rho \ell$$

with $k_{\nu}^{-} \gg k_{\nu}^{+}$, integrated over the width of $I(\sigma^{+})$ and $I(\sigma^{-})$ where the width (FWHM) is about 1/10 of FWHM of absorption profile. Here ρ is the density of mercury seen by the 2537-Å monitoring light in the absorption cell. The organic sample containing mercury was placed in the heated furnace ($T \approx 800^{\circ}\text{C}$ to 1200°C) in the presence of O_2 blown into the furnace at a constant rate, decomposed, and transferred to the absorption tube. The rate equation that governs the time variation of the decomposition of material in the absorption cell can be written as $[dN(t)]/dt = \xi - RN$, where N is the number of Hg atoms at time t , ξ is the production rate of mercury due to sample decomposition, and RN is the rate of loss of Hg from the absorption path (due to the conversion of host material from solid to gas, and carrier gas). By preparing the furnace environment so that the sample decomposes at a constant rate, we get $N(t) = (\xi/R)(1 - e^{-Rt})$, where R is the flow rate out of the absorption tube section. R contains flow due to O_2 injection as well as gas evaporated from the host material. The integral of $N(t)$ over time represents the total mercury present in the host material. Thus, as long as we let the R be the same for the calibration sample as well as for the unknown to be measured, we can expect to obtain accurate results. This can be satisfied, e.g., by flowing a large amount of a carrier gas such as O_2 . This behavior was verified against samples furnished by various organizations. The sample used as a standard,

furnished by the NBS, is supposed to contain 0.2 ppm; the sample is orchard leaves, and is the only standard available, though tentative. This was compared with a solution of HgCl which we prepared, and the results were similar. Using this internal consistency to calibrate our instrument, we measured the samples furnished by other organizations. Table I shows typical measurements, using our technique as well as others.

Recently³ we reported on a similar technique using the hyperfine (AI·J) structure coupled with the Zeeman effect for ¹⁹⁹Hg. Because of the complex energy-level structure of ¹⁹⁹Hg it was necessary for us to use more complex procedures to utilize two optical components for detecting Hg and non-mercury. Use of the even isotope clearly simplifies the analysis of the technique.

We believe that our experimental results shown in Table I indicate that the isotope-shifted Zeeman-effect technique is quite powerful, and as far as we know, no existing technique can match its rapid detection time. Another advantage of this technique is that no chemical separation of the trace element to be measured is needed prior to the atomic absorption detection. This is the source of uncertainty in all the conventional techniques used today. Thus, the uncertainty in our device is connected with the evaporation problem, which is relatively simple when compared to the complex chemical problems involved in other methods.

Although an article of this type may not be appropriate

matter for the Physical Review Letters, we feel that there are many techniques of atomic physics that can be applied directly to the important problems in environmental research. This is the reason for the submission of our article to this journal.

We would like to thank R. D. McLaughlin for preparing samples and testing the instrument during the developmental stage; Eric Gagulitz of the National Marine Fisheries Service, Seattle, Washington, for his interest in the instrument and for furnishing us with samples; Dr. Peter Lerke of the National Cannery Association for their calibrated fish samples; Will Berlund for the construction of lamps; and Mitchiyuki Nakamura for electronic design assistance and Doug MacDonald for wiring the electronic circuits.

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- * Work supported by U.S. Atomic Energy Commission.
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Figure Captions

Fig. 1. Zeeman-shifted line profile of σ^+ and σ^- of ^{198}Hg in 7 kG, superimposed on an absorption profile of naturally-occurring mercury in 1 atmosphere (STP) of N_2 .

Fig. 2. Experimental arrangement.

Fig. 1

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Fig. 2

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