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DISCLAIMER

A TRACE ELEMENT DETECTION METHOD BASED ON COHERENT SCATTERING OF RADIATION[*]

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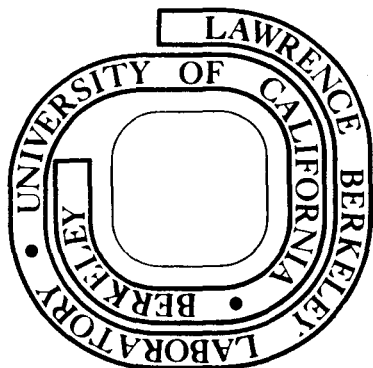
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The detection and measurement of trace

quantities of mercury in air by a magneto-optic

coherent forward scattering technique is described.

The method is characterized by high sensitivity

and selectivity, and is applicable to a broad class

of elements.

Although coherent light sources are being employed for environ-

mental research, various widely investigated coherence phenomena in

the scattering of light by atoms have not yet been applied to the detec-

tion of trace atmospheric pollutants. Series and his collaborators[1,2]

have pointed out that in a vacuum, resonance radiation is coherently

scattered forward by atoms when a magnetic field is applied ex-

ternally. The forward scattered signal as a function of magnetic field

strength is called a "line-crossing,"[2] in analogy to a level-crossing

in laterally scattered light. During the extension of line-crossing mea-

surements to mercury atoms in an atmosphere of argon or nitrogen,[3]

we observed that the sensitivity for detection of the forward scattered

signal was comparable or superior to that for atomic absorption mea-

surements on the same sample. We report here a further extension

of these measurements to mercury atoms in air, under conditions that permit the direct detection and measurement of mercury occurring in molecular or particulate form.

The apparatus used in these measurements (Fig. 1) includes the lamp shown mounted in a magnetic field, chosen to Zeeman-shift[4] the σ resonance lines to optimize the forward-scattered signal.[5] These lines could be separately selected with a $\lambda/4$ plate. However, in the measurements reported here, the isotope shift of mercury atoms at zero field was used instead to maximize both the absorption[4] and forward scattering.[5] This was accomplished with an electrodeless discharge of the mercury isotope 204. The 2537 Å intercombination resonance line was focused through a Glan-prism polarizer and a windowless stainless steel furnace of length L, which was resistance heated to about 900°C. This temperature is sufficiently high to dissociate all mercury compounds. A second prism polarizer blocked the unscattered incident light. When a longitudinal magnetic field was applied to atoms in the detection region within the furnace, the differential dispersion associated with the Zeeman-split, Lorentz-broadened and -shifted absorption of the airborne atoms rotated the plane of polarization of the forward scattered light.[3] A fraction of this scattered light consequently passed the analyzer to the 1P28 photomultiplier detector. An interference filter with passband centered near 2737 Å was used to block stray radiation emitted by the heated furnace; otherwise, wavelength selection was unnecessary. The furnace tube (L = 3/4 m long, 1 cm^2 cross-sectional area) was placed inside a solenoid of equal length. However, no power supply to produce a mean field strength above 2.8 kG was available. Optimum detection

sensitivity for naturally abundant mercury in air occurs at a field strength near 7 kG. [5]

The expression for the detected signal at the optimum field strength, as a function of atom density N, is[1,5]

$$S(N) \propto 2(\alpha NL)^2 (1 - 4\alpha NL) \qquad (1)$$

where α is a constant that depends on atomic parameters. This equation is an approximation valid at low atom density N, the region of interest here. The fundamental dependence on N^2 is characteristic of coherence phenomena; absorption, which enters in the third power at low levels, is expressed by the final factor in parenthesis. Consequently effects of absorption on the forward scattered signal, either by mercury or by molecules with absorption bands at the same wavelength, are relatively minor as long as the total absorption is low. We have verified this with a vapor mixture of benzene and mercury. [5] The benzene vapor alone produces a strong absorption, but no forward scattered signal.

To measure calibrated low concentrations of mercury vapor in air, with a syringe we withdrew a measured amount of carefully mixed mercury vapor from a closed container holding a pool of mercury at a uniform temperature of 0°C. This vapor was diluted by filling the syringe with laboratory air and the entire contents injected into the furnace through a hypodermic needle. The accuracy of this method has been calibrated against standard dilute liquid samples containing mercury, inserted in a slightly different manner. [5,6] A continuous flow of argon carrier gas was maintained through the furnace, which mixed and diluted the standard sample.

As shown in Fig. 1, the furnace is composed of a mixing volume V_m and a detection volume V_d. When $V_m = V_d$, under assumptions of sudden sample injection and complete mixing,[6] the dependence of the forward-scattered signal on time t and on the injected atom number N_0 is

$$S(N, t) \propto (N_0/V_d)^2 \, (t/t_m)^2 \, e^{-2t/t_m} \tag{2}$$

if absorption is completely neglected. The time at which the signal maximum occurs is denoted t_m. Figure 2 shows examples of signals and superposed normalized plots of Eq. (2). Small departures from the theoretical expression at long times indicate that mixing in the detection region is probably not complete. The non-linear dependence of the signal on atom density is evident. Insertion of the measured parameters into Eq. (2) for an observed minimum detectable peak signal gave a sample density in the detection volume of 0.3 $\mu g/m^3$. If the longitudinal magnetic field were increased to 7 kG, this could be reduced by another factor of 3, well below the proposed federal guideline for ambient air[7] of 1 $\mu g/m^3$. Industrial atmospheres have permissible levels to 50 $\mu g/m^3$. Such atmospheres could be passed continuously through the furnace without dilution.

In an unheated furnace, the same initial atom number yields a signal about $\frac{1}{25}$ as large as that obtained with a heated furnace. This effect can be due either to mercury bonded in molecular or particulate form, or to the condensation of atoms on the walls of the cold furnace; either effect in a mercury detector without a heated furnace must lead to erroneous determinations.

Finally, we note that with this same apparatus, conventional atomic absorption measurements of mercury atom density can be made simply by rotating the analyzer parallel to the polarizer, and turning the longitudinal field strength to zero. Based on the signal-to-noise ratio, we found that detection by atomic absorption was only one-tenth as sensitive as by forward scattering. The difference in sensitivity could have resulted in part from excessive lamp noise, since the lamp was not temperature controlled. Nevertheless, the immunity of forward scattering to this type of noise source is impressive.

In summary, coherent forward scattering offers an alternative to atomic absorption as a selective, sensitive technique for detecting trace quantities of elements in air. Forward scattering is also relatively insensitive to small quantities of interfering absorbing background molecules and the ease of converting the apparatus to an absorption monitor points the way to straightforward compensation techniques if larger interfering backgrounds are present.[5] Since unscattered radiation from the light source is automatically blocked, no dispersive elements are required in the system.

We are indebted to R. Diamond and to R. Davis for the loan of essential apparatus.
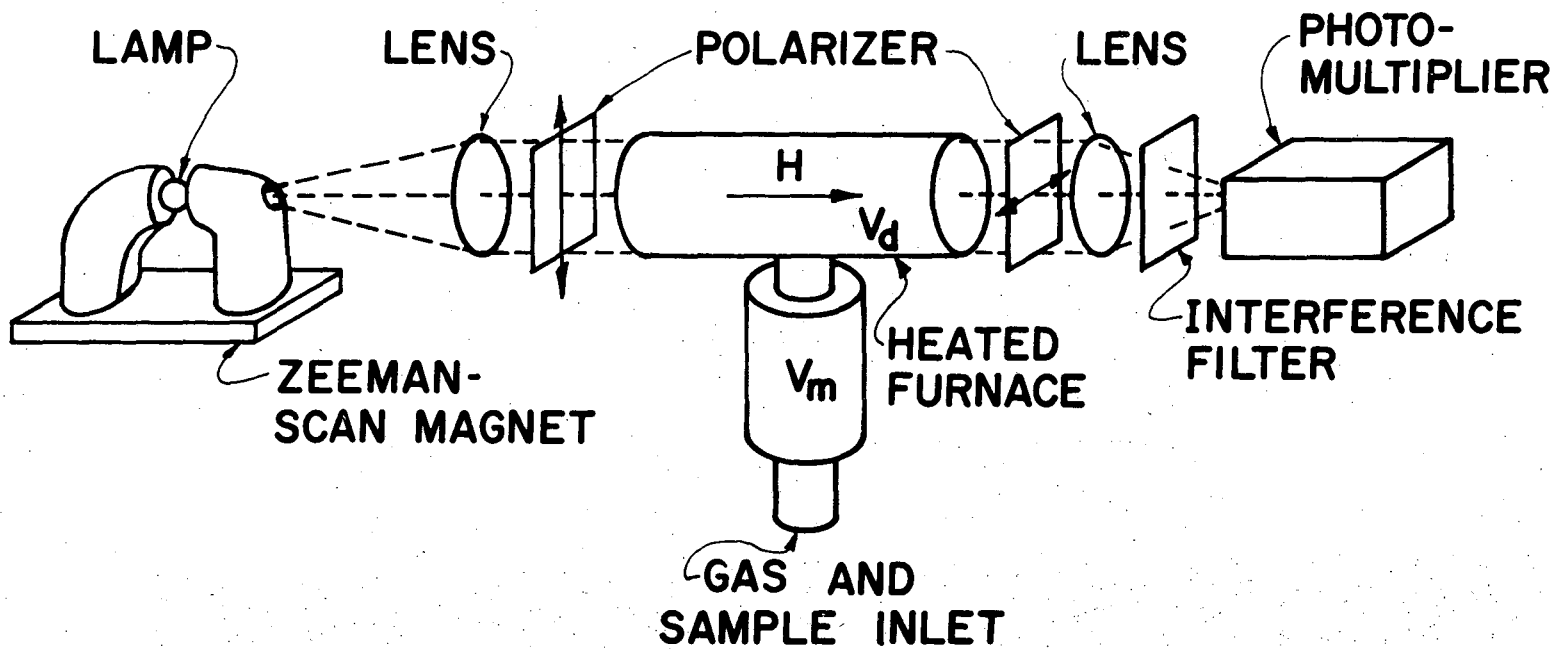
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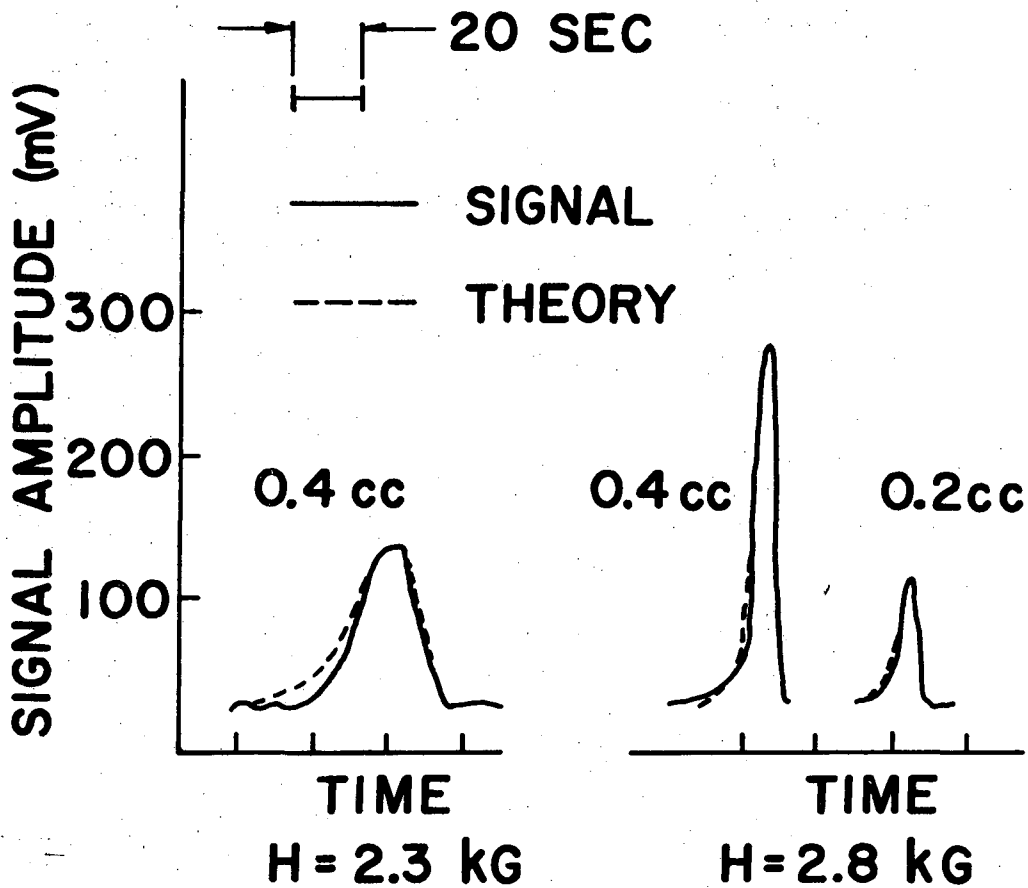
Figure Captions

Fig. 1. Schematic diagram of the apparatus used in the forward scattering measurements. The furnace is surrounded by a solenoid which produces the longitudinal field H. For these measurements, the field on the lamp was zero.

Fig. 2. Forward scattered signals produced by indicated volumes of mercury Hg vapor in air samples injected into a stream of argon carrier gas. The signal at the left was measured with lower field strength but also with slower carrier gas flow rate than those at the right.

LAMP   LENS   POLARIZER   LENS   PHOTO-MULTIPLIER

H

V_d

V_m

ZEEMAN-SCAN MAGNET

HEATED FURNACE

INTERFERENCE FILTER

GAS AND SAMPLE INLET

-8-

XBL 7310-1266

Fig. 1

Fig. 2

XBL 7310-1265