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ABSTRACT

We have demonstrated that the isotope-shift Zeeman-effect atomic-absorption (IZAA) spectrometer, originally developed for the direct measurement of trace elements in solid and liquid samples, now has sufficient sensitivity for continuous monitoring of the total mercury concentration in ambient air. Improvements in this technique described here increase its sensitivity by more than a factor of 100; this allows the detection of a minimum mercury concentration of 0.2 $\mu g/m^3$, one fifth the proposed federal standard for ambient air.

The proposed federal standard for the maximum allowable mercury concentration in air to which the general public may be exposed is one microgram per cubic meter.[1] At present, convenient techniques do not exist to continuously monitor the total mercury content of air at this level. We report a series of measurements which demonstrate that the isotope-shift Zeeman-effect mercury detector 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 without previous chemical separation of the Hg from the host material.[2,3] 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 consisting of two constituents; one has a wavelength centered on the absorption profile of natural mercury in air, while the other is slightly displaced (less than 1 cm^{-1}) from the mercury absorption line. The absorption of the centered constituent is due to mercury vapor as well as to non-mercury decomposition products - particulates (smoke) as well as any thermally stable molecular species present; the absorption of the displaced constituent is due only to the non-mercury background. In the vicinity of the 2537Å line of mercury, this background absorption does not change significantly over 1 cm^{-1}. Consequently, by taking the difference in the absorption of the two constituents, one measures the absorption due to mercury alone.

The heart of the technique lies in the method by which the probe and the reference constituents are generated, and the mode by which one distinguishes the one from the other; here improvements have been made over earlier versions of the technique. In the present apparatus (see Figure 1) both constituents are supplied by a single ^{204}Hg lamp operated in a 15 kilogauss magnetic field. When such a lamp is viewed perpendicular to the applied magnetic field, the Zeeman effect splits the 2537Å intercombination line ($6^3P_1 \rightarrow 6^1S_0$) into three components: a σ^- component shifted to longer wavelength, a σ^+ component shifted to shorter wavelength, and an unshifted π component.

Now the mercury present in the absorption tube consists of a naturally occurring mixture of several stable isotopes. Since the absorption tube is operated at one atmosphere, the absorption lines of each isotope are Lorentz broadened, and shifted towards longer wavelength. In Figure 2 we plot the resulting total absorption profile due to naturally occurring mercury at one atmosphere of N_2; superimposed upon this profile is the Zeeman-split emission spectrum of the ^{204}Hg lamp. Note that the π component corresponds accurately to the peak of the absorption profile of the natural mercury, while the σ components are both well off on the wings of the profile. Consequently we may use the differential absorption of the π and σ components as a measure of the quantity of mercury present in the absorption tube--the π component becomes the probe beam, and the σ components taken together become the reference beam.

Another feature of the Zeeman effect provides a convenient means of separating the π and the σ components. At right angles to the magnetic field, both σ components are linearly polarized perpendicular to the field, whereas the π component is polarized parallel to the field. Since this means that the σ and the π components are polarized perpendicular to each other, either component may be viewed independent of the other with a properly aligned linear polarizer. So, the isotope shift along with the Zeeman effect supplies one with both probe and reference beams and an easy means of discriminating between them.

Of course, in order to utilize the full power intrinsic to this technique, one must employ some method of alternately allowing the probe and then the reference beam to be transmitted through the absorption region. A device was contructed which electrically accomplishes this beam switching; it exploits the optical properties of fused quartz. When fused quartz is stressed, it becomes birefringent--that is, light polarized along the stress axis propagates through the quartz at a different velocity than light polarized perpendicular to the stress axis. If a plate of fused quartz is oriented so that the stress axis makes an angle of 45° with the plane of polarization of incoming light, the birefringence of the quartz introduces a phase shift proportional to the applied stress between the two perpendicular components of the light. By appropriately choosing the stress, the quartz can be made to function as a quarter-wave or half-wave plate.

In the present instrument, a plate of fused quartz is oriented at 45° with respect to the magnetic field applied to the light source. The quartz is mounted within a split C-frame pulse-transformer core on which is wound a driver coil. Since the length of the quartz plate is chosen to leave an air gap of 0.5 mm on one side of the split core, varying the current in the driver coil varies the stress on the quartz plate. So the device becomes a current-controlled variable phase-retardation plate.[4]

This device is followed by a linear polarizer oriented parallel to the light-source magnetic field. When the current applied to the variable phase plate is zero, the polarizer passes only the π, or mercury probe component of the light; when the current is adjusted so that the quartz is a half wave plate, the quartz rotates the plane of polarization of both the π and the σ components by 90°, - so now the polarizer passes only the σ, or reference components. As a result, the combination high-magnetic-field lamp, variable phase plate, and linear polarizer make up a light source the wavelength of which can be electrically switched between discrete values at a frequency of several hundred Hertz.

The light next passes through the absorption tube and then into a .25 meter Ebert monochromator which has sufficiently low resolution that it transmits both components equally well. If no mercury is present in the absorption tube, the σ and π components are absorbed and scattered identically by the non-mercury background, and hence the output of the spectrometer phototube is unmodulated; in the presence of mercury however, the π component will be more strongly

absorbed than the σ components, and so the spectrometer output will vary at the audio frequency at which the switching from the one component to the other takes place. This in-phase audio component of the phototube output is extracted and amplified by a lock-in amplifier.

In practice, in order that the lock-in amplifier output be proportional to the quantity of mercury present in the absorption tube, two additional devices are necessary. The first is an amplifier with electronically-controlled gain following the photomultiplier; its gain is automatically adjusted to compensate for the attenuation of the transmitted light by non-mercury constituents and for variations in the intensity of the light source. The second is a quartz polarization-compensator plate--simply a piece of quartz anywhere along the light path oriented at an angle with the light beam. By varying the angle, one can compensate for accidental differences in the intensity of the probe and reference components--which mimic the presence of mercury in the absence of any sample. This accidental partial polarization comes about because a) any reflective surface--such as the lamp envelope--which is not both flat and normal to the direction of propagation introduces a partial polarization[5], and b) excitation by electron impact which is not totally isotropic causes alignment of the excited state and partial polarization of the decay radiation.[6]

The claim that under the conditions described above, the output of the lock-in amplifier is proportional to the quantity of mercury in the absorption tube can be justified mathematically. One can

derive the following expression for V_p, the output signal of the phototube:

$$V_p \simeq C \left[I_0(\pi)\exp(-\ell \int(k_\pi+k_s)d\nu) \quad \sin^2 \frac{\omega t}{2} \right.$$

$$+ \left\{ I_0(\sigma^+)\exp(-\ell \int(k_{\sigma+}+k_s)d\nu) \right.$$

$$\left. \left. + I_0(\sigma^-)\exp(-\ell \int(k_{\sigma-}+k_s)d\nu) \right\} \quad \cos^2 \frac{\omega t}{2} \right]$$

Here C is a constant accounting for the gain of the multiplier and for geometry factors; $I_0(\pi)$, $I_0(\sigma^+)$ and $I_0(\sigma^-)$ are the initial intensities, and k_π, $k_{\sigma+}$, and $k_{\sigma-}$ are the absorption coefficients due to natural mercury in the absorption tube of the π, σ^+ and σ^- components respectively; k_s (which is assumed to be the same for all three components) is the broad-band attenuation coefficient due to non-mercury constituents, ℓ is the length of the absorption tube, and ω is the angular frequency of the modulation applied to the phase-retardation plate.

Making use of the conditions that $\ell\int k_\pi d\nu$, $\ell\int k_{\sigma+}d\nu$, $\ell\int k_{\sigma-}d\nu \ll 1$, that $k_\pi \gg k_{\sigma+}, k_{\sigma-}$, and that the polarization compensator plate is adjusted so that $I_0(\pi) = I_0(\sigma^+) + I_0(\sigma^-)$ we find

$$V_p \simeq C\, I_0(\pi)\exp(-\ell \int k_s d\nu) \quad \left\{ (1-\frac{\ell}{2}\int k_\pi d\nu) \right.$$

$$\left. - (\frac{\ell}{2}\int k_\pi d\nu) \cos \omega t \right\}$$

The automatic gain control compensates for attenuation due to non-mercury constituents represented in the factor $[\exp(-\ell \int k_s d\nu)]$, so the input signal to the lock-in amplifier depends only upon the absorption due to mercury. Since $(\int k_\pi d\nu) \propto \rho$ (density of Hg), the modulated component is proportional to the density of mercury in the absorption tube; the output of the lock-in is, of course, proportional to this component.

To test the sensitivity of the IZAA spectrometer, a simple procedure was used to obtain a known concentration of mercury vapor. Approximately 1 cc. of mercury was placed in a septum-covered test tube which was maintained at 0°C by an ice bath. The sample consisted of air and mercury vapor inhaled by a syringe which penetrated the septum; care was taken to inject as much air as was to be withdrawn to avoid creating a partial vacuum. After withdrawal from the test tube, the remaining volume in the syringe was filled with air in order that the total volume of gas in each sample remain the same. Then the sample was injected into the expansion chamber of the furnace [the leg of the "T" in Figure 1; see Figure 2 of Reference 3 for the shape of the thermal reaction section]. In this chamber, the mercury vapor mixes with argon continuously flowing at 6.8 ml/sec at S.T.P. 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. Secondly, 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. The expression for the quantity of mercury in the tube, $N_A(t)$, is given by

$$N_A(t) = \frac{N_0 V_A}{(V_0 - V_A)} \left\{ \exp\left(-\frac{Rt}{V_0}\right) - \exp\left(-\frac{Rt}{V_A}\right) \right\}$$

where N_0 is the quantity of mercury injected into the expansion chamber, 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. In our case V_0 = 100 ml, V_A = 38 ml and R = 6.8 ml/sec at S.T.P. On the basis of these two checks we conclude that the calculated concentrations are at least accurate to within a factor of two.

Figure 3 presents the results of one series of measurements made at low concentration. In Figure 3a, the peak concentrations (calculated from our expression for $N_A(t)$) for the three curves are respectively 11, 1.1 and 0.55 μg of mercury per cubic meter. In Figure 3b, we plot peak height versus volume of mercury vapor injected into the furnace; it illustrates that indeed, over the range of 0 to 11 $\mu g/m^3$ concentration, the response of the instrument is linear with concentration. Measurements were extended to a calculated concentration of 66 $\mu g/m^3$, with no apparent deviation

from linearity. Peak area versus concentration was also plotted with essentially identical results. From these measurements one can estimate that the minimum detectable concentration of mercury for this equipment used in the mode described above is at least 0.2 $\mu g/m^3$.

Several straightforward improvements can be expected to markedly improve this sensitivity. One can use the 1849Å resonance line of mercury instead of the 2537Å line; this should increase the sensitivity by a factor of 50 because of the larger absorption cross section. The use of this line without complication by self-reversal is possible since the lamp operates near room temperature, and since the inside diameter of the portion of the lamp from which light is accepted is only about 1 mm. Conversion from pulsed to continuous sample injection offers yet further opportunity to enhance the sensitivity since then much longer integration times can be used.

In conclusion we note that the basic advantages of the IZAA technique are:

1. Only one light path and one photodetector are used to monitor both mercury and the non-mercury background. This greatly simplifies problems with accidental polarization and with gain-drift of the photodetector.
2. The apparatus has no moving parts; the new type of polarization modulator allows the modulation frequency to be as high as several hundred Hertz. This order-of-magnitude increase in frequency provides much better background cancellation than was possible in earlier

versions of this technique.

3. With the furnace at 1000°C, total mercury content--that is both mercury vapor and mercury compounds incorporated into particulates--will be detected. Of course, one may choose to run with the furnace cold and to monitor only mercury vapor.

We wish to acknowledge the work of Doug MacDonald in mechanical design, Willy Berlund in the construction of light sources, and that of Berken Chang, Don Nelson and Chuck Dols in the initial development of the current-controlled variable phase-retardation plate.

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REFERENCES AND FOOTNOTES

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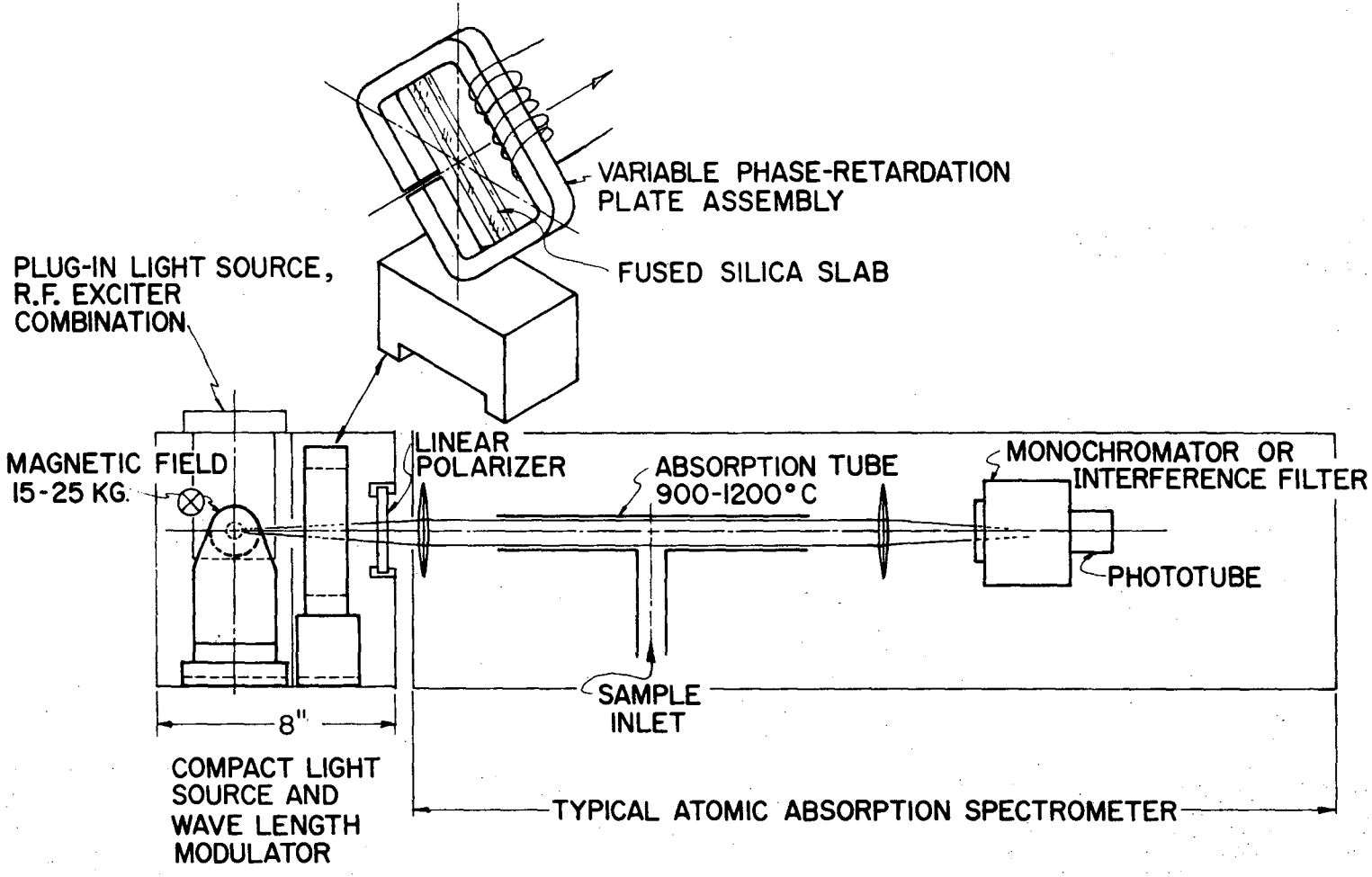
FIGURE CAPTIONS

Figure 1 Schematic diagram of the IZAA Spectrometer as used in the present experiment.

Figure 2 The continuous curve is a plot of the absorption profile of naturally occurring mercury in N_2 at S.T.P. The lower, superimposed curves give the emission spectrum of a ^{204}Hg lamp operated in a 15 kilogauss magnetic field.

Figure 3 a) Curves 1, 2, and 3 are plots of Lock-in amplifier output versus time for pulses of gas containing 11, 1.1, and .55 μg of mercury per m^3 admitted at time t = 0.

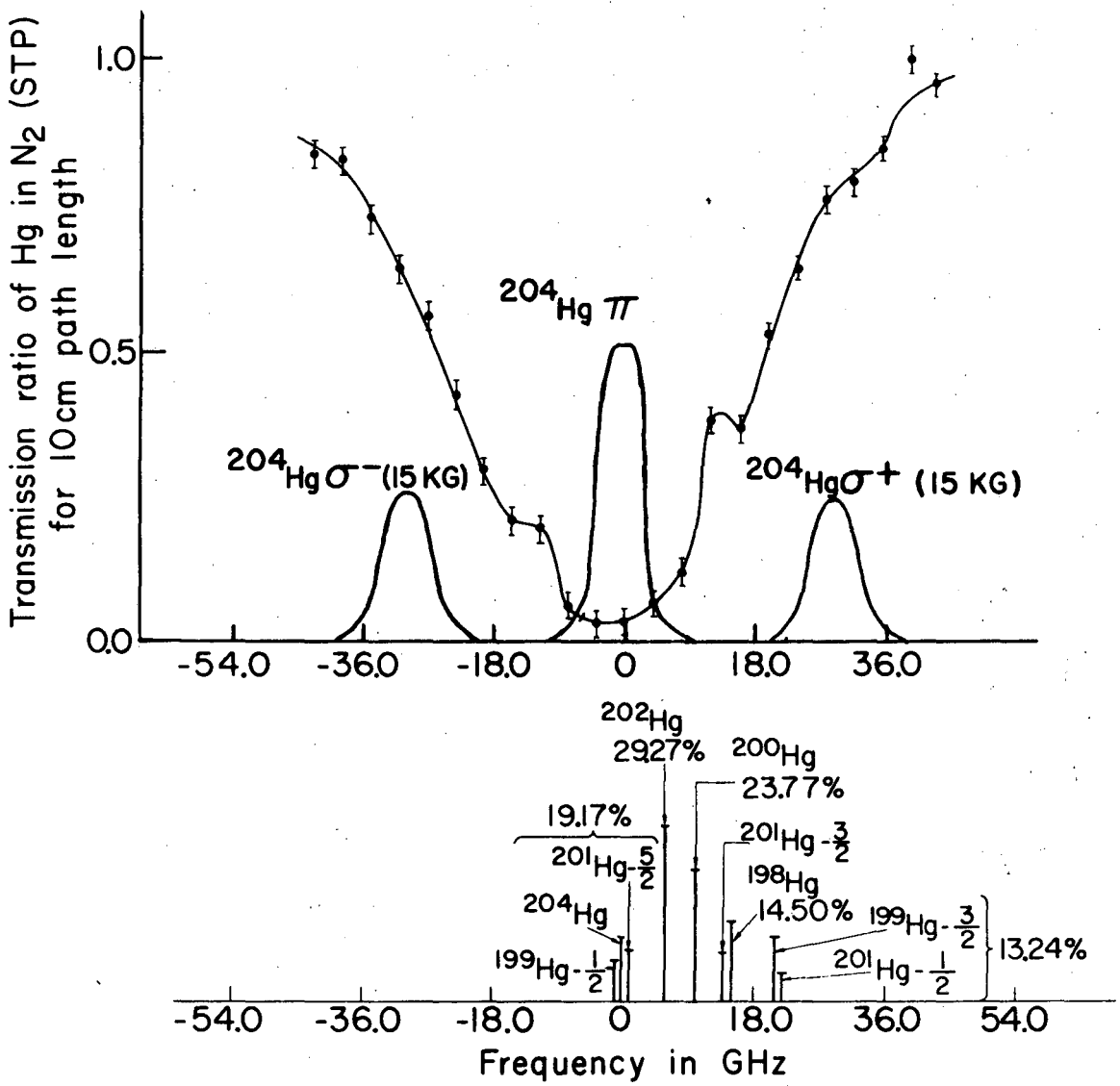
b) The pulses were provided by injecting known volumes of mercury vapor at S.T.P. into the instrument. The plot gives peak height versus volume of injected mercury vapor. The concentration range is 0 — 11 $\mu g/m^3$.



OPTICAL ARRANGEMENT FOR ISOTOPE-SHIFT
ZEEMAN-EFFECT ATOMIC ABSORPTION SPECTROMETER

XBL 731-104

Fig. 1



XBL 731-105

Fig. 2

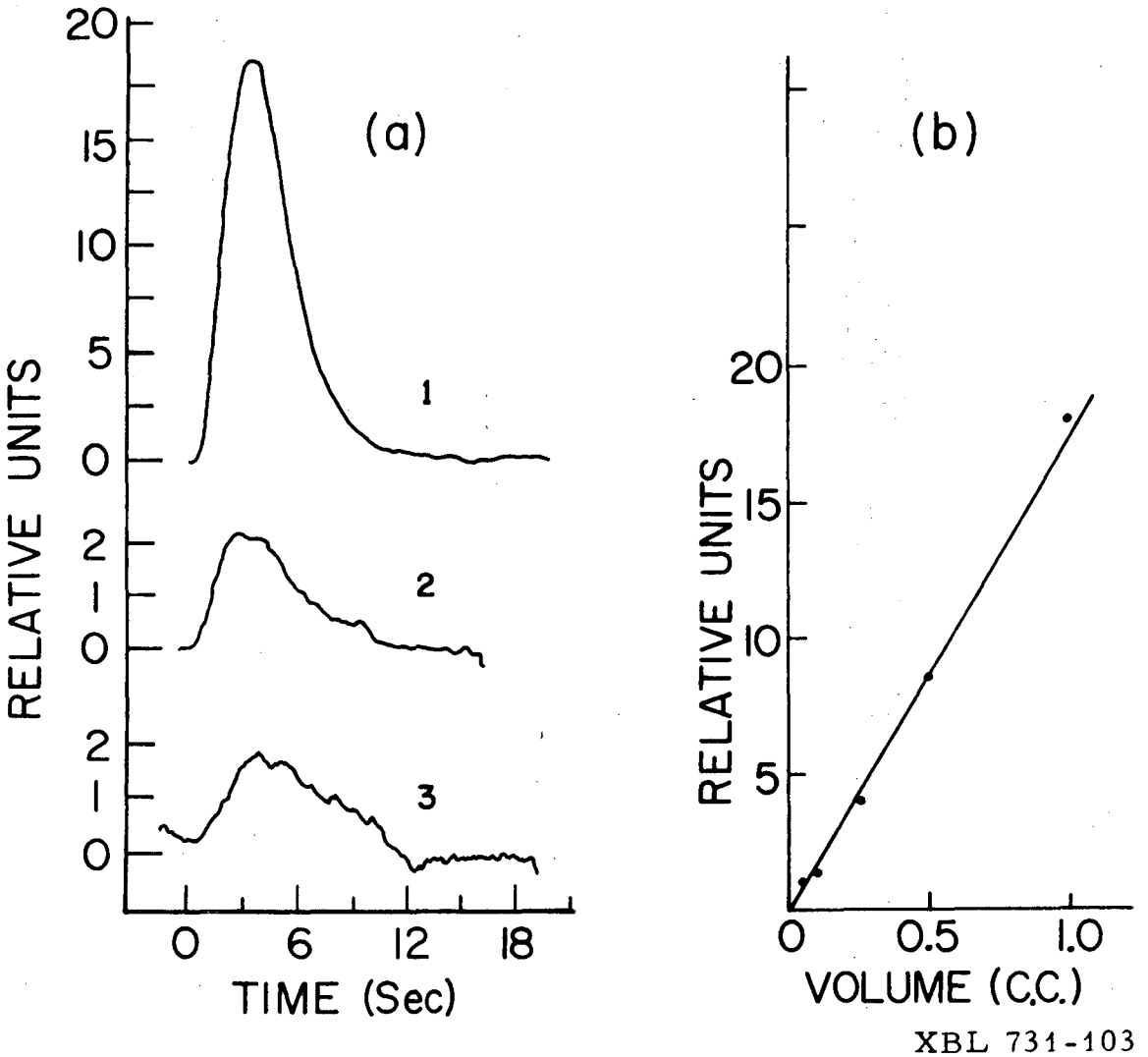

(a)
(b)
RELATIVE UNITS
TIME (Sec)
VOLUME (C.C.)
1
2
3
0
6
12
18
0.5
1.0
5
10
15
20
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Fig. 3

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