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### Authors

Hadeishi, T.  
Mclaughlin, R.D.

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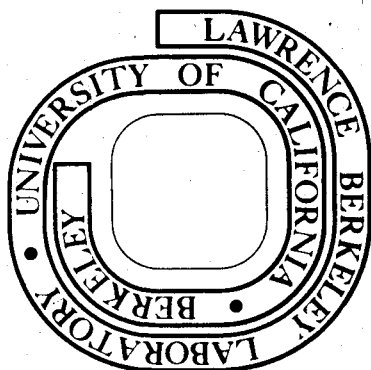
IZAA  
A NEW APPROACH TO CHEMICAL ANALYSIS

T. Hadeishi and R. D. McLaughlin

May 1975

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IZAA

A NEW APPROACH TO CHEMICAL ANALYSIS

T. Hadeishi and R.D. McLaughlin

Energy and Environment Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

May 1975

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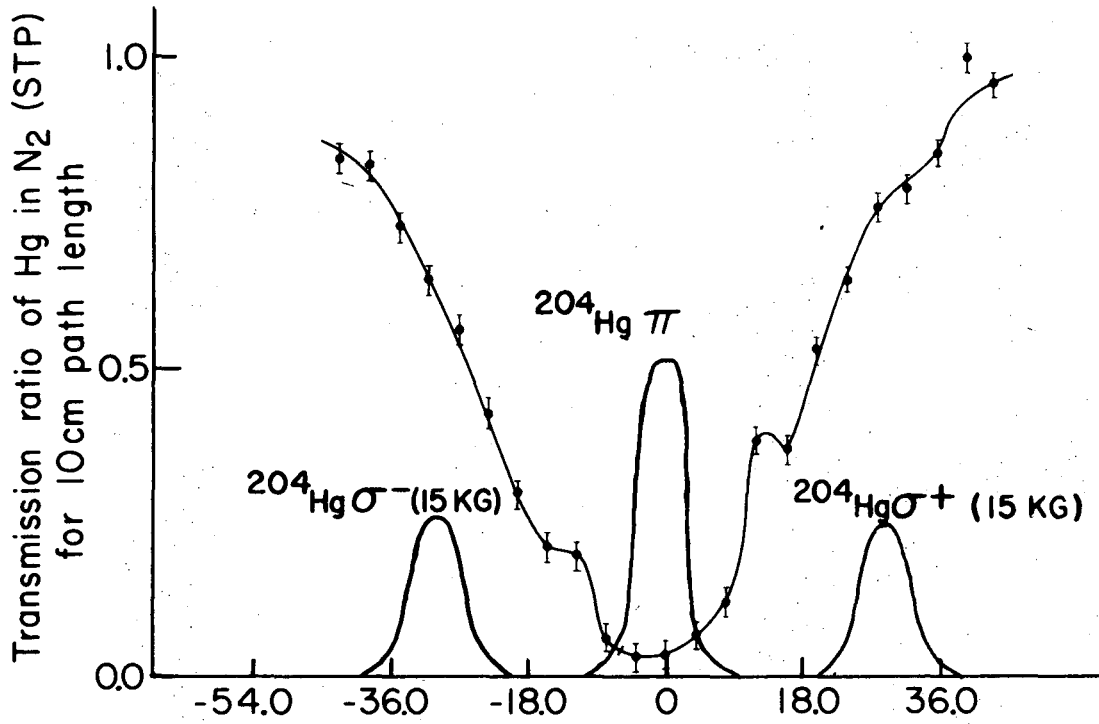
## IZAA

## A NEW APPROACH TO CHEMICAL ANALYSIS

T. Hadeishi and R.D. McLaughlin

A technique will be described in this paper that, we believe, will revolutionize the field of analytical chemistry when it is exploited to its full potential. This technique allows one to insert a biological sample into a hot furnace and determine the amount of Hg, Cd or Pb that was in the sample by shining a light beam through the smoke and vapors that come off while the sample burns. This approach requires no chemical treatment of the sample and after insertion into the furnace the result is obtained in less than one minute. This technique represents an extension of the atomic absorption method so that much more extreme conditions are necessary before interferences become a problem. The ability to tolerate larger amounts of potentially interfering substances results from a procedure of continuously correcting for these materials as the sample burns. This is done by using a light source that has been placed in a magnetic field so that the resonant line is split into its Zeeman components as shown in Figure 1.

This figure depicts the absorption profile of the Hg 253.7 nm line as it appears in nitrogen at a pressure of one atmosphere. The width of the line is due to the pressure broadening of the hyperfine components of the natural Hg line. This same figure shows the relative positions of the Zeeman components of the Hg 253.7 nm line due to the single isotope  $^{204}\text{Hg}$  in the presence of a



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Figure 1

magnetic field of 15 KG. The splitting at this wavelength is about  $1/8 \text{ \AA}$  or  $2 \text{ cm}^{-1}$ . The basic idea of Isotope Zeeman Atomic Absorption Spectroscopy (IZAA) is to use the outer  $\sigma$  components to monitor the presence of smoke and vapors in the light beam and the inner  $\pi$  component to monitor the presence of the element of interest; in this case Hg. To do this, use is made of the fact that the planes of polarization of the  $\sigma$  components and the  $\pi$  component are oriented at  $90^\circ$  with respect to each other.

Figure 2 diagrams the instrumentation required to preform this continuous correction. The optical components of the instrument consist of an electrodeless discharge tube placed between the poles of a permanent magnet, an electro-optical device used to rotate the planes of polarizations of the  $\pi$  and  $\sigma$  Zeeman components, a linear polarizer, a furnace that causes combustion and atomization of the sample, appropriate lenes, wavelength isolation device and phototube. The planes of polarization of the Zeeman components are rotated by the use of a variable phase retardation plate.<sup>1</sup> This device consists of a quartz plate clamped inside a C frame of a transformer core on which is wound a driven coil. The length of the plate is chosen to leave an air gap of 0.5 mm in one side of the split core. By varying the current in the coil a stress is applied to the quartz plate which causes it to become birefringent. Light polarized along the stress axis propagates through the quartz at a different velocity than light polarized perpendicular to this axis. The plate is oriented so that the stress axis makes an angle of  $45^\circ$  with the

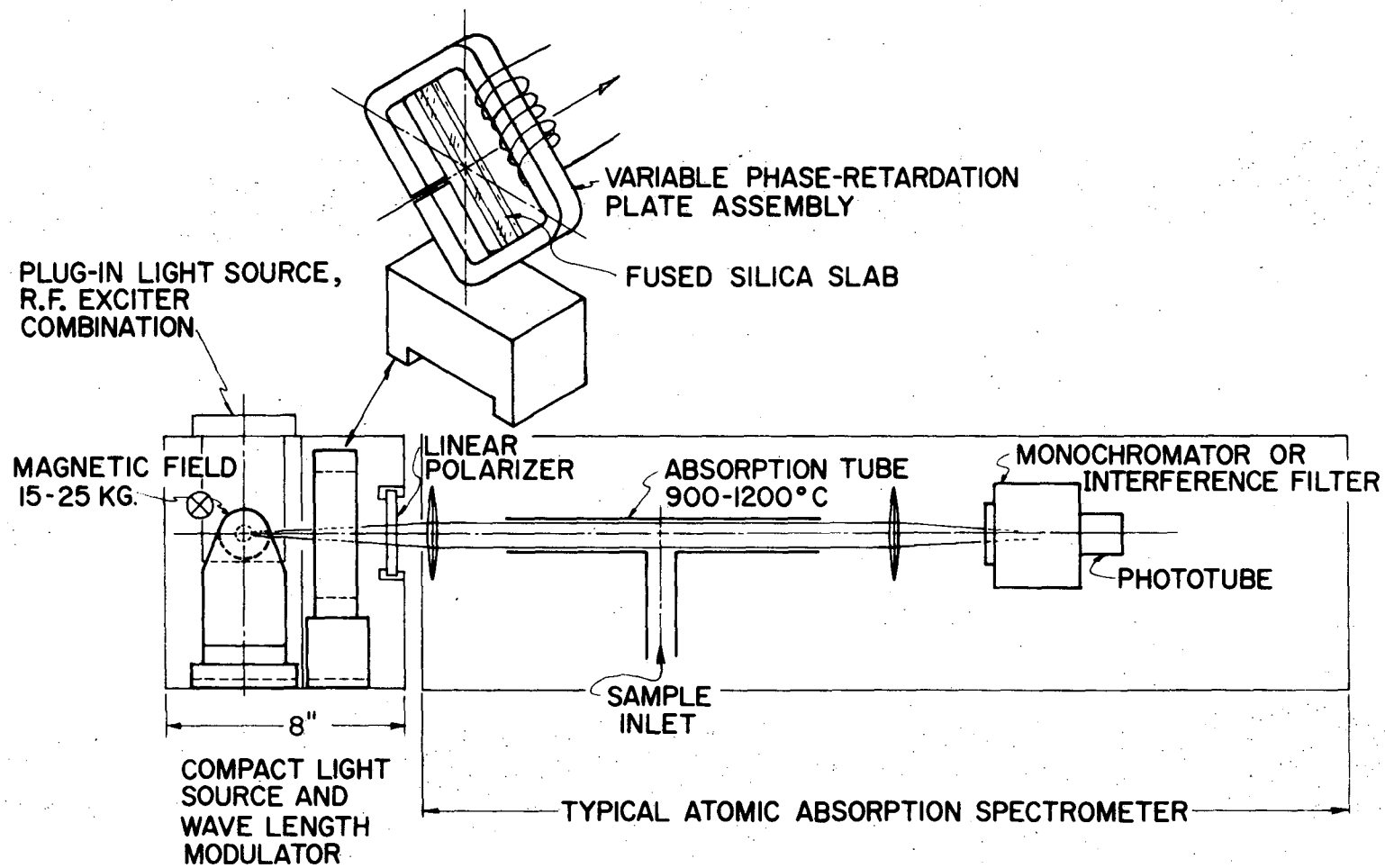


Figure 2



plane of polarization of the incoming light. As a result, the plane of polarization of the  $\pi$  and  $\sigma$  components are rotated as the current is increased through the driving coil on the transformer core.

A linear polarizer positioned in front of this assembly allows light of one and then the other polarization to be transmitted in a sinusoidal manner. As a result of this optical arrangement, species that have a continuous absorption over the  $1/8 \text{ \AA}$  interval of 253.7 nm cause a change in light intensity falling upon the phototube that depends on the rate of arrival and departure of these species in the light beam; whereas the presence of Hg atoms in the light path results in a sinusoidal signal which varies at the same frequency as is used to drive the variable phase retardation plate. These two different types of intensity variations are distinguished by electronically processing the phototube output as shown in Figure 3.

The output is first fed through an automatic gain control circuit which electronically varies the gain to automatically compensate for the attenuation of the transmitted light by the non-Hg constituents and for variations in the intensity of the electrodeless discharge tube lamp. The output next is processed by a lock-in amplifier which amplifies the variation in voltage that occurs at the same frequency as is used to drive the retardation plate. This amplified voltage is used to charge a capacitor to a voltage that is monitored by a digital voltmeter. The reading on the digital

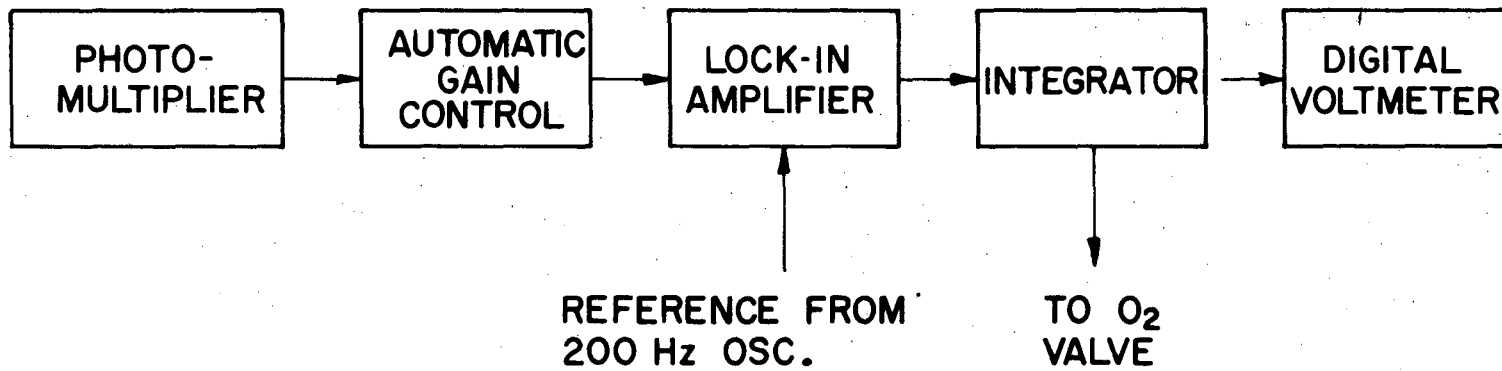


Figure 3

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voltmeter is directly related to the amount of Hg in the sample.<sup>2</sup> Although this system remains operative as long as the light intensity is not diminished by more than 80% or so, a point is eventually reached where the ability of the AGC to compensate for the diminished light intensity is exceeded and meaningful results can no longer be obtained. The furnace is designed to minimize the production of absorbing smoke and vapors so that relatively large amounts of sample may be used without this point being reached. One type of furnace design is pictured in Figure 4.

This furnace consists of two chambers<sup>3</sup>: a combustion chamber and an absorption chamber. For Hg determinations the furnace is held at a temperature of about 900°C, and oxygen is continuously flowed through the furnace. The ideal is to totally convert the organic material to carbon dioxide and water since neither of these gases adsorb appreciably at 253.7 nm. The larger the sample that can be introduced the greater the sensitivity of the instrument. The instrument now can detect as little as 0.2 ng of mercury and, depending upon the sample type, the order of 50 mg of sample can be used without causing too great an attenuation of the light level. This results in a sensitivity of 4 ppb for direct burning of samples. In order to insure sufficient oxygen for total combustion the sample temperature is raised above the flame point in a chamber of large volume (30 ml). Although this does make the combustion process more efficient it also causes a tail to appear on the plot of Hg signal vs time.<sup>4</sup> This makes it difficult for

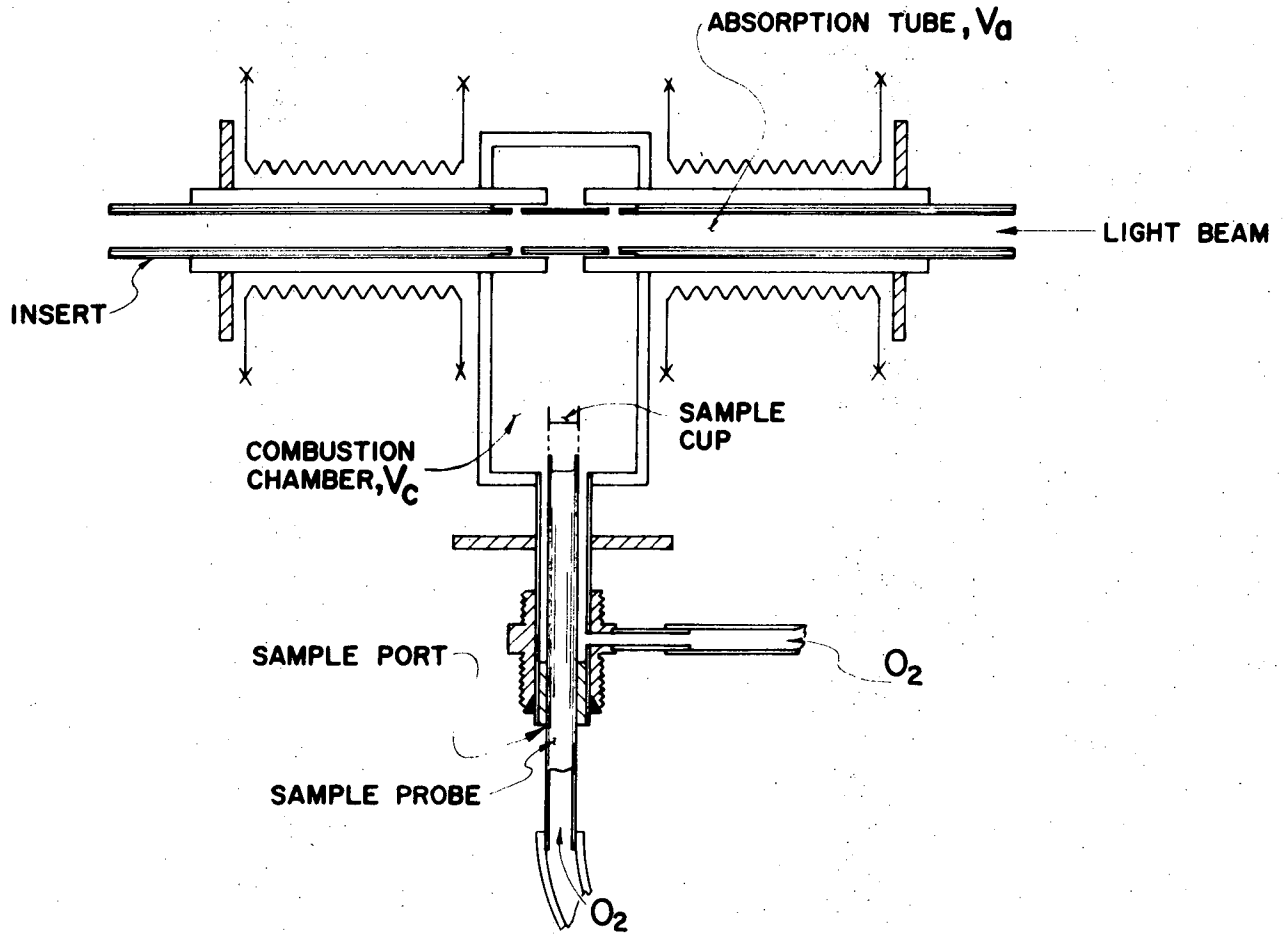


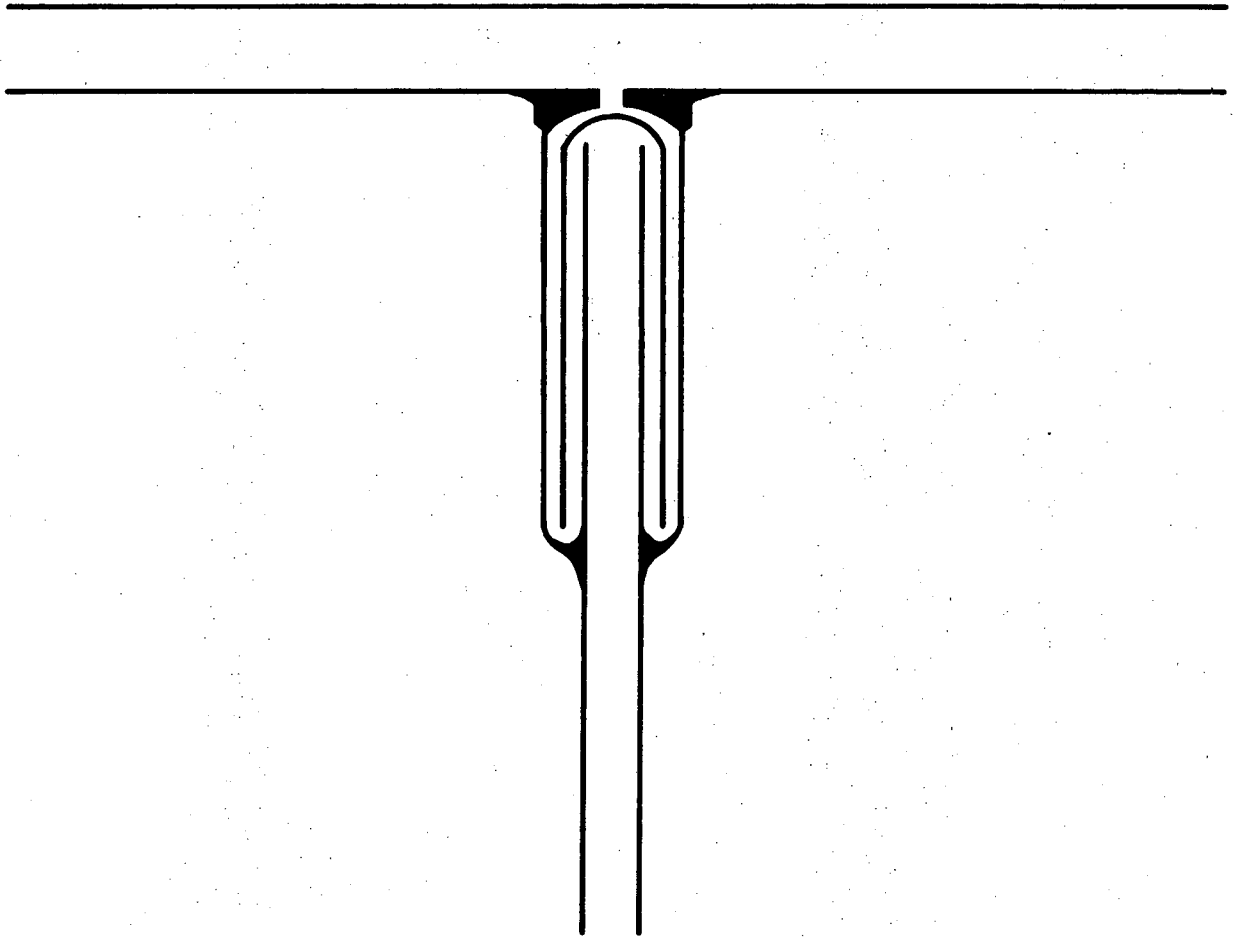
Figure 4

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the operator to know when to stop the intergration process. In order to lessen this problem another design was utilized which is pictured in Figure 5.

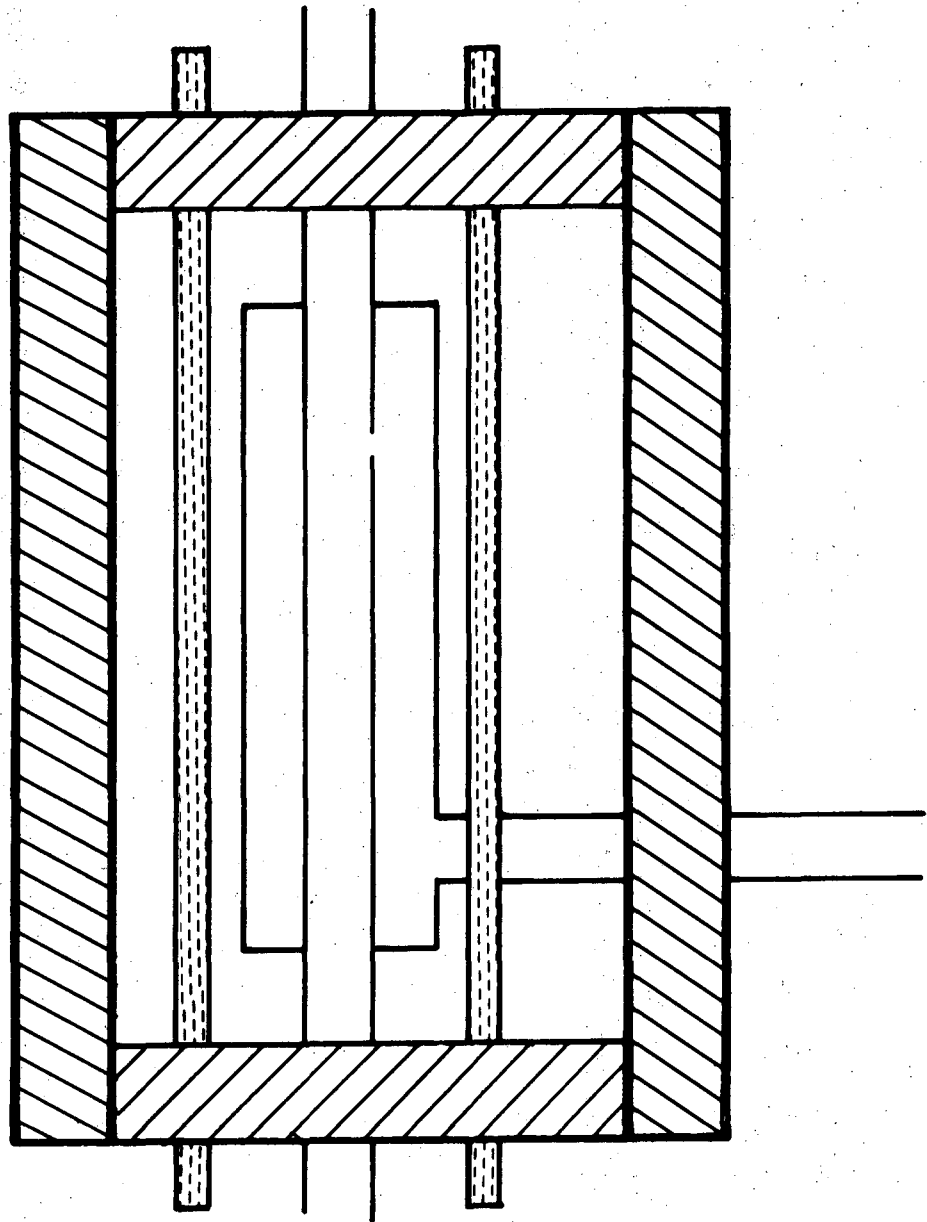
This furnace approximates a tube preceding an absorption chamber rather than two chambers. As soon as combustion occurs the products are swept over a long path to raise the temperature as much as possible and then into the absorption chamber. This does solve the tailing problem but combustion is not so efficient. In order to achieve the higher temperatures necessary for Cd and Pb a furnace of a different design was used, (See Figure 6).

In this case a furnace made of fire brick with Si C heating elements was utilized. Whereas the earlier furnaces were constructed from stainless steel, it was now necessary to use Ni quartz or  $Al_2O_3$ . Ni and quartz seem to be the better since these materials are more resistant to thermal stress. For ease of construction, the combustion chamber is now concentric with the absorption chamber and more recent models have a window over the end that is farthest from the entrance port. Preliminary results indicate that for Cd and Pb this furnace acts as a one stage gas chromatograph. In order to achieve atomization pyrolysis occurs in a flowing stream of hydrogen. The volatile pyrolysis products rapidly progress through the furnace but the Pb or Cd require 10 to 15 seconds before they appear in the absorption chamber. It appears that the same mechanism allows for the insertion of rather large (1/2 ml) volumes of solution. The characteristics of this



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Figure 5



XBL755-2971

Figure 6

furnace are still being determined.

Table 1 compares the analytical capability of the Atomic Absorption Technique with the Isotope Zeeman Atomic Absorption Technique. Although the flameless AA method has better lower limits of detection it is not possible to use large volumes of samples with this method because of interference effects. In terms of relative sensitivity the IZAA method is already superior and the potential of this method has not been exploited to the degree that has occurred for AA techniques. To relate this sensitivity to present analytical needs the tentative E.P.A. drinking water standards are also included (in units of ppb).

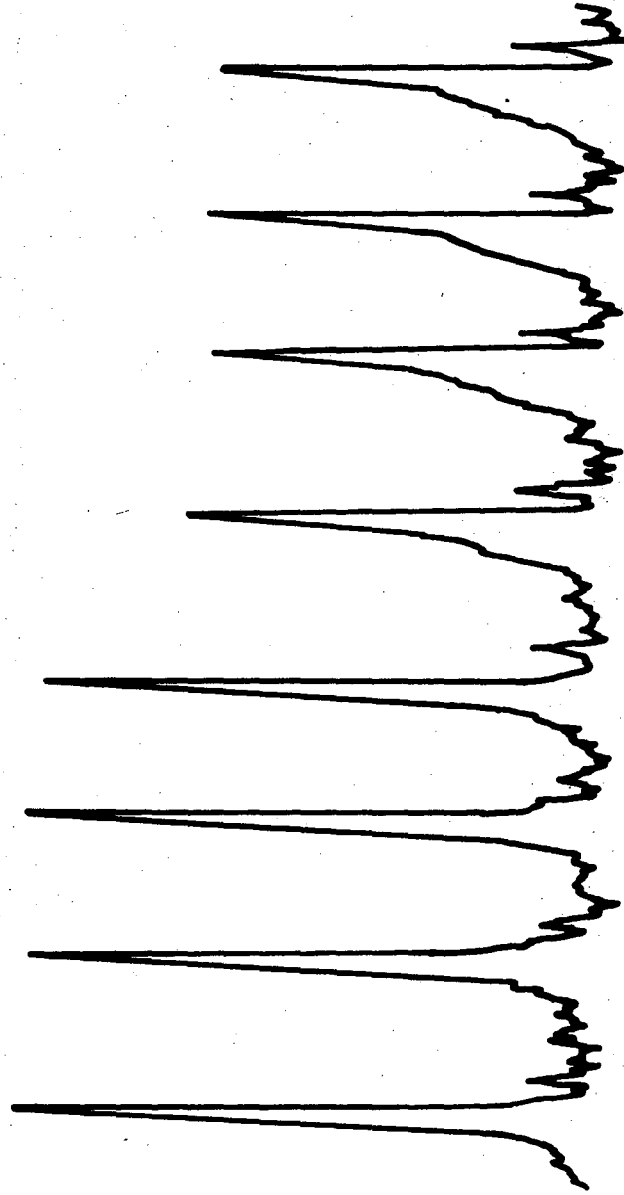
An example of the application of this technique to the analysis of a 3% NaCl solution is illustrated in Figure 7. The solution was chosen to duplicate the interference problem caused by sea water. Time increases from right to left. The broader peaks on the right result from 10 ng of lead in 20  $\mu$ l of salt solution. The narrow peaks on the left result from 10 ng of lead in 10  $\mu$ l of 1% HNO<sub>3</sub> solutions. We believe the tailing of the salt solution peaks results because lead is contained in molten NaCl after the water evaporates and thus comes out more slowly. The average integration value for the salt solutions was 197 with a 3.69% coefficient of variation. The average integration value for the 1% HNO<sub>3</sub> solutions was 202 with a 2.4% coefficient of variation.



TABLE I

## SENSITIVITY OF AA COMPARED WITH IZAA

Element	Wavelength	LLD $\mu\text{g/ml}$	Flameless		IZAA		Drinking Water Standards (ppb)
			pg	ppb	pg	ppb	
Cd	228.8	0.005	0.6	0.6	10	0.1	10
Hg	253.6	0.5	350	350	100	2	2
Pb	217.0	0.01	7	7	200	2	5
	283.3						



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Figure 7

Summary

We have tried to present a picture of a new analytical technique that has great potential. Much remains to be done in the development of this method for other elements and the methods of combustion and pyrolysis for different types of sample matrix.

Efforts are presently underway to develop a variation of this technique for the detection of molecules.

Acknowledgment

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5. "National Interium Primary Drinking Water Standards", Fed. Reg. 40 (51) (1975).

## FIGURE CAPTIONS

- FIGURE 1: Comparison of emission lines from  $^{204}\text{Hg}$  discharge in magnetic field with absorption line of natural Hg at pressure of one atmosphere
- FIGURE 2: Electro-optical components of IZAA
- FIGURE 3: Electronic components of IZAA
- FIGURE 4: Furnace assembly for combustion of samples for Hg analysis
- FIGURE 5: Furnace design to prevent "tailing" of Hg signal
- FIGURE 6: Furnace design for Pb and Cd determinations
- FIGURE 7: Comparison of lead signal from 3% salt solution with standard solution.

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