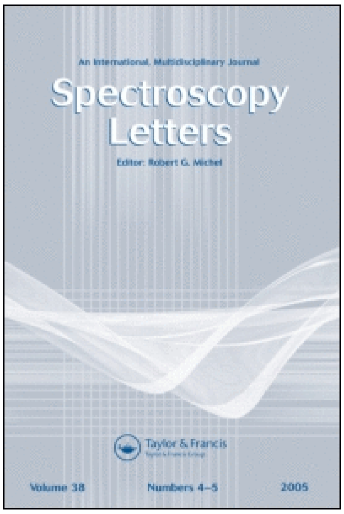

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THE CONTINUOUS DETERMINATION OF LEAD IN AIR

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Metallic pollutants are of major concern in present pollution studies. The high level of lead concentrations in automotive emissions has attracted the attention of the federal government and to the manufacture of internal combustion engines. Our cities suffer from rising levels of lead in their atmosphere. Ambient air in Los Angeles contains three micrograms of lead per cubic meter. In heavy traffic concentrations have been reported ranging from 14 to 44 micrograms per cubic meter. Concentrations of 1 to 3 $\mu g/m^3$ have been reported in the outlying and commercial districts respectively, in Cincinnati and Philadelphia (1). Paris has reported 3.3 to 9.8 $\mu g/m^3$ on her streets (2). Osaka, Japan reported 4.5 $\mu g/m^3$ in residential levels, 9.9 $\mu g/m^3$ in factory districts, 10.0 $\mu g/m^3$ in main traffic arteries and 36.0 $\mu g/m^3$ in dense traffic (3).

The U.S. Public Health Service has taken air samples inside plants and has reported 11 milligrams/m^3 inside insecticide plants, 38 milligrams/m^3 inside storage battery plants and 49 milligrams/m^3 inside paint factories (4).

Present methods of lead analysis utilize a method of scrubbing large volumes of air, either by physical entrapment of particulates or by chemical collection of molecular lead. These methods are characterized by delay and pollutant averaging and necessitate highly skilled personnel.

Physical trapping methods involve passing air through various filtering media such as filter paper (5,6,7,8), fiber glass sheets (9, 10), millipore filters (1,11), membrane and microsorban filters (12,13).

Chemical agents utilized have been iodine in methyl alcohol (14,18), iodine in aqueous podassium iodide (17,20), iodine in carbon tetrachlride, iodine monochloride, iodine crystals (19), and dilute nitric acid solutions (15,16).

Analytical methods utilized have included x-ray fluorescence (11), amperometric titrations (21), polarography (9,20,23,28) spot tests using tetrahydroxy-p-benzoquinone (6), H_2SO_4 (7), paper chromatography (5), emission spectroscopy (8,15,16,24,25,27) and colorimetry using dithionate (19,20,27).

The advent of atomic absorption as developed by Walsh (29) introduced new possibilities for accurate analysis at low sensitivities. The absorption of radiation by an element is proportional to the number of absorbing atoms in the light path. An increase in the number of atoms in the light path will result in an increase in absorption and therefore in analytical sensitivity.

Long absorption tubes have been previously utilized to improve sensitivity (30,31,32,33,34). These long path tubes serve to concentrate the cloud of atoms being produced and to hold them in the light path for an increased period of time. Robinson reported a sensitivity to 0.0013 ppm for lead with a T-shaped quartz flame adaptor (35). Kiortyohann reported a value of 0.02 ppm as the detection limit of lead (36).

Kind and L'vov have studied furnaces that operate at high temperatures (38). Sensitivities in the range of 10^{-8} to 10^{-11} grams have been achieved. Woodriff has employed a long absorption tube and high temperature furnace, reporting a sensitivity of 5.7×10^{-11} g (39,40).

The flame atomizer, commonly used in atomic absorption, has a poor efficiency for producing neutral atoms from most samples; only one in 10^6 atoms which pass through the flame are reduced (37).

EQUIPMENT

The atomization step utilizes hot carbon rods and CO to reduce the lead compounds to the atomic state and the equipment was designed to take advantage of long path absorption tubes to accumulate atoms in the light path.

Radiation Source: Demountable hollow cathode lamp (42) utilizing a shielded cathode with Jarrell Ash 82-500 power supply.

Monochromater: Jarrel-Ash 82-500 1/2 meter monochromator with 8 speed scanning attachment. 100 μ fixed slits.

Detector: R.C.A. 1P28 photomultiplier.

Amplifier: Jarrel-Ash 82-000.

Recorder: Beckman model 10005, 10 inch stripe chart recorder.

The graphite rods were heated with a Lepel 5000 watt radio frequency generator using 4 inch graphite rods and a 7 turn 5½ inch copper coil. Heating of the quarts "T" was accomplished by 1000 watt nichrome resistance heaters.

The air sample which contained lead was passed over the white-hot carbon rods. The lead was reduced to neutral atoms which passed into the heated absorption chamber. Here their concentration was measured by atomic absorption. The effluent from the apparatus was removed through the exhaust ports. The air sample was introduced on a continuous basis (Figure 1).

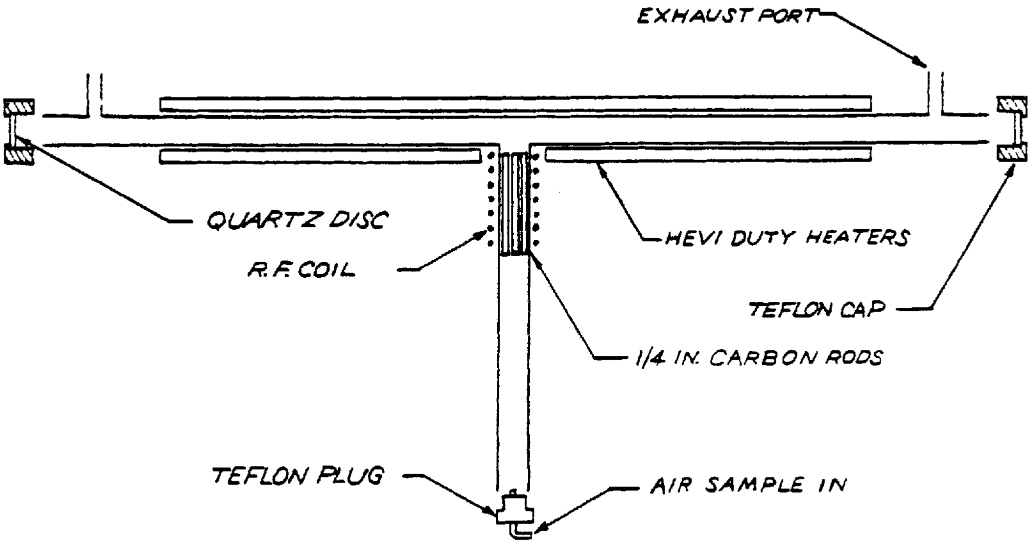

FIGURE 1
ABSORPTION TUBE

Calibration Data

The calibration of the apparatus was accomplished utilizing the method of Altshuller and Cohen (43). This method involved the diffusion of tetraethyl lead from a tube of known diameter and path length into an air stream of known velocity. A diagram of the apparatus is shown in Figure 2. Each device was calibrated by weight loss over a period of days or weeks. The data were used to calibrate the absorption apparatus. The rates for the lowest concentrations were extrapolated from tubes of the same path length, but of larger diameter. The ratio of diffusion rates then equals the ratio of the cross sectional areas (43). Table I gives the diffusion rates and concentrations. The calibration of the instrument is shown in Figure 3 and Table II. The precision of the method is shown in Table III.

Sensitivity Limits

The sensitivity limits for 1% adsorption can be calculated from Table II. It was observed that the 1.5 μg/m resulted in 9% absorption.

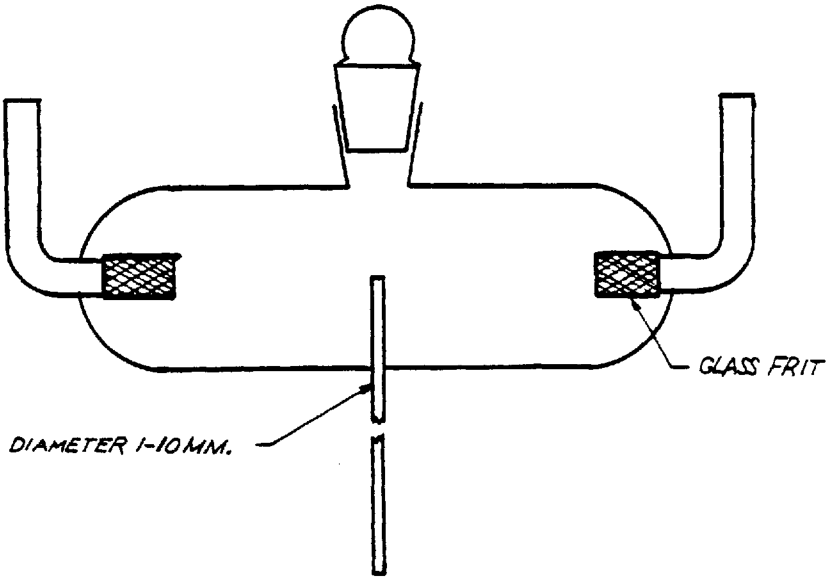

FIGURE 2
DIFFUSION CHAMBER

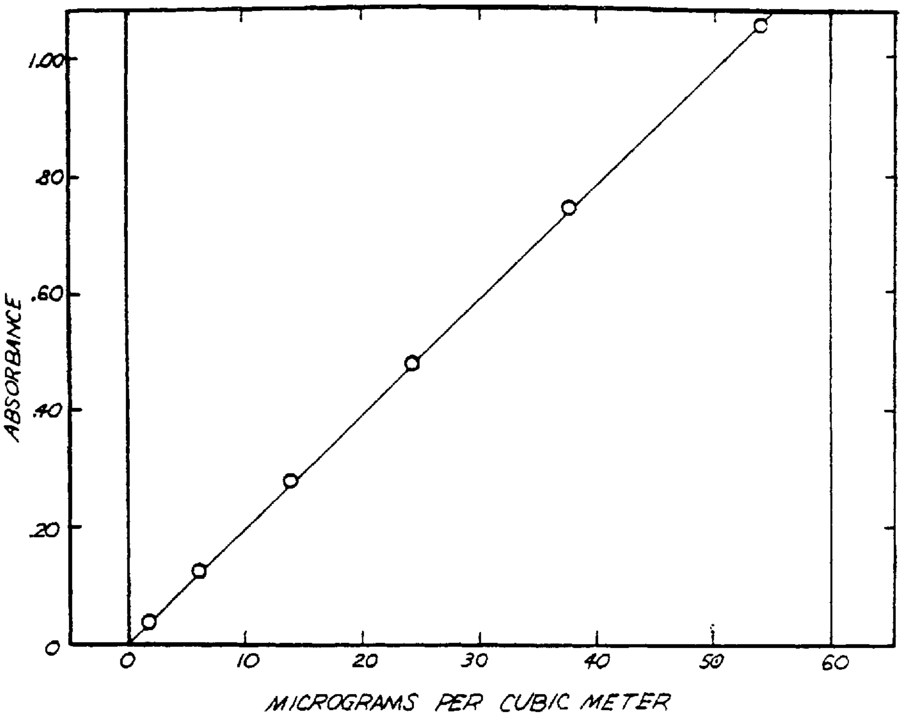

FIGURE 3

TABLE I

CALIBRATION OF THE DIFFUSION APPARATUS

Diameter of Diffusion Tube	Weight Loss min^{-1} by diffusion µg/min	Resultant Concentration when diffusing into air. Stream flowing 1.200l/min. $\mu g/m^3$
0.99	0.0018	1.5
2.00	0.0072	6.0
2.99	0.0162	13.5
4.05	0.0238	29.0
5.09	0.0450	37.5
5.95	0.0650	59.0

TABLE II

CALIBRATION OF ABSORPTION

Concentration	% T	Absorbance
1.5	90.9	0.041
6.0	74	0.130
13.5	53	0.276
24.0	33	0.481
37.5	18	0.745
54.0	8	1.100

Further, the volume of air observed in the light path at any one time was about 160 ml. Based on these observations it can be calculated that the sensitivity limits obtained were:

Sensitivity in air = $0.16\ \mu g/m^3$

Absolute sensitivity (total lead) = 3×10^{-11} g

TABLE III

REPRODUCIBILITY OF THE METHOD

Concentration 6.0 $\mu g/m^3$ Pb

Sample No.	% T	Absorbance
1	74	.131
2	74	.131
3	73	.136
4	74	.131
5	75	.125
6	74	.131
7	73	.136
8	74	.131
9	74	.131
10	74	.131

It is anticipated that with better instrumentation and more optimised conditions that these levels can be substantially reduced.

Determination of Lead in the Atmosphere

Several determinations were performed using air in the laboratory as an analytical sample. Ambient air was passed through a small diaphragm compressor. The results are given in Table IV. They indicated that lead was detectable even on this non-optimised equipment. With more sophisticated equipment, it is anticipated that significantly better sensitivity will be achieved.

Confirmation of Absorption by Lead in the Atmosphere

It was necessary to prove that the absorption of the lead resonance lines was caused by lead in the sample and not some other unknown

TABLE IV

DETERMINATION OF LEAD IN LABORATORY AIR

Date	Absorbance	Concentration Pb
8-5-69	.040	1.4 μg/m^3
9-2-69	.300	15.0 μg/m^3
10-14-69	.068	2.8 μg/m^3
11-7-69	.050	2.0 μg/m^3

material either atomic or molecular. Two approaches were taken.

(1) Removal of lead from the air entering the instrument. This resulted in a loss of absorption at 2833Å and indicated that the lead was the absorbing element.

(2) Measurement of absorption at near-by non-absorbing lead lines. Any absorption would be evidence of molecular absorption rather than atomic absorption. No such absorption was observed. The procedures are discussed with more detail.

(1) <u>Removal of Lead from the Air</u>

Several scrubbing agents were investigated. The most efficient was activated charcoal. Two scrubbers filled with activated charcoal were utilized; one was attached to the air supply from a compressed air tank used previously to supply air for calibration and interference studies. A second scrubber was inserted into the air stream between the injection apparatus and the absorption tube, in such a manner that it could be by-passed easily. With the scrubber in the line essentially no absorption was observed. When the scrubber was removed from the line 26% absorption was registered, consistant with a concentration of the 6.0 μg/m^3 lead which was injected into the airstream.

A similar run was performed with the air supply tank scrubber and yielded a value which varied from tank to tank from 37.6 to 1.0 $\mu g/m^3$. Lead free air samples were prepared by scrubbing the air supply line with a charcoal scrubber.

A series of similar determinations using iodine and iodine based scrubbers after the injection point demonstrated a similar ability to remove most if not all of the lead in the air stream. However, molecular absorption by iodine in the absorption tube was observed in these cases. As a result, charcoal was chosen as the scrubbing agent.

(2) Measurement of Non-Absorbing Lines of Lead

The absorption due to a 6.0 $\mu g/m^{-3}$ lead sample was measured at the resonant wavelengths 2170Å and 2833Å, which yielded transmittances of 42.1% and 74% respectively. The obvious choice for analytical sensitivity would be the 2170Å line. However, due to its low intensity, the level of amplification necessary introduced a high noise level on the detector. Measurements were also made at the near-by 2176Å and 2806Å lines. The absence of absorption at these lines indicated that the absorption at 2833Å and 2170Å was due to lead in the tube and not an extraneous molecular species.

Interferences

By utilizing a modulated light source, excitation and radiation interferences were not observed.

It has been shown that molecular fragments from organic compounds can cause interferences in flame atomizers (44). Although the normal concentration of organic compounds in the atmosphere do not approach levels encountered using flame atomizers and organic solvents, a study was performed to determine the effects of organic compounds on the developed method.

The pure organic liquid was injected into the air stream at a rate sufficient to give a concentration of 100 mg/m^3. The sample stream also contained 6.0 μg/m^3 of lead. The results are given in Table V. No interferences were observed from the organic compounds noted. But the occurance of equal absorbance at resonance and non-resonance lines for the halogen compounds indicated molecular absorption had taken place. However, these compounds are not usually present at levels as high as 100 mg/m^3 in the atmosphere and should not provide a source of serious error in the analysis of air pollutants.

Chemical interferences caused by incomplete reduction of molecules to ground state atoms or the formation of refractory oxides are a major of interferences in atomic absorption and emission when flame atomizers are used. The anions PO_4^{3-} and CO_3^{2-} cause a reduction in the absorption of lead (45) when samples are run from aqueous media.

A Nichrome resistance heater of 800 watts was constructed and placed into the air stream five inches upstream from the atomizer. Power was supplied through an eight ampere Powerstat transformer. This heater was calibrated as to temperature with a Chromel-Alumel thermocouple.

Porcelain boats were filled with lead phosphate, carbonate or chloride and separately placed into the airstream within the heater. The boat was heated until a reasonable and reproducible absorption signal was obtained. Both the signal and Powerstat settings were noted.

The heater was removed from the analytical stream and placed within a hood. Air was passed through the heater at the same rate as the analytical stream.

The boats containing the various chemical forms of lead were carefully weighed and one by one placed into the heater where the temperatures corresponding to the absorption signals were reproduced. The

TABLE V

INTERFERENCE EFFECTS OF ORGANIC COMPOUNDS

This Table shows change in % absorption from the normal value for a sample 6.0 $\mu g/m^{-3}$ effected by organic solution.

Compound	2170	2976	2833	2803
water	0	0	0	0
n-butyl alcohol	0	0	0	0
isopropyl alcohol	0	0	0	0
n-butyl amine	0	0	0	0
n-butyl sulfide	0	0	0	0
nitrobenzene	0	0	0	0
pyridine	0	0	0	0
acetonitrile	0	0	0	0
carbontetrachloride	38	39	20	19
chloroform	22	23	12	11
benzene	0	0	0	0
toluene	0	0	0	0
bromotoluene	8	7	5	6
methyl iodide	12	11	9	8
heptane	0	0	0	0
hexane	0	0	0	0

boats were weighed weekly until an accurate difference weighing could be made.

In determining the weight loss one could then calculate the concentration of lead released into the air stream. The absorption and weight differences were compared (Table VI). No evidence of chemical interferences could be detected due to phosphate, carbonate, or chloride anions.

TABLE VI

INTERFERENCE EFFECTS OF ANIONS

Anion	Absorbance	Concentration Dtn. by wt. loss $\mu g/m^3$	Concentration Dtn. by Absorption $\mu g/m^3$
Phosphate	.4102	20.96	21
Carbonate	.3213	16.31	16
Chloride	.5824	29.87	30

CONCLUSIONS

This method seems to provide a rapid, sensitive, and reproducible method for the continuous determination of atmospheric lead. The lower limit of sensitivity was observed to be about 3×10^{-11} g of lead.

This method appears to be applicable to a wide variety of metals and their determination is presently under investigation.

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