Determination of Airborne Particulate Lead by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Lead in air and biological materials may be measured by dithizone methods. These methods suffer from pH dependency and instability of developed colours. Polarography may be used, but unless the test sample is very carefully prepared to eliminate all traces of organic materials, the lead wave may be masked and lead thought to be absent. Methods using anodic stripping voltammetry show promise but more practical experience must be obtained. The sensitivity of methods using emission or X-ray spectrography is low and the accuracy is affected by matrix error. A limit of identification of 0.1μg of lead is reached by using the Weisz ring oven (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at a suitable wavelength and the lead is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The lead levels found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the concentrations of airborne particulate lead found in either ambient or industrial atmospheres. The method is not applicable to the measurement of lead compounds in vapor form, such as tetraethyl or tetramethyl lead. The method may be readily adapted to the measurement of tetraethyl lead in gasoline. As airborne particulate lead may make up 1 to 5% of airborne particulate matter, analytical sensitivity is ordinarily not a problem. Based upon the flame mode, washed glass filters and a nominal air sample volume of 2,000 cubic metres, lead is measurable to 0.010 micrograms per cubic metre. A slight improvement in sensitivity results from the use of cellulose filters, or down to 0.0075 micrograms per cubic metre. For the same test sample, the use of the flameless mode increases the sensitivity considerably.

3. PRINCIPLE

A prepared test sample, containing the inorganic constituents in aqueous acidic solution, is reduced in the flame or graphite furnace to the atomic state. The amount of the element of interest is measured by making use of its property of absorbing light of its characteristic frequency when in the atomic state.

4. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample in acidic media to form a homogeneous test sample. As microgram quantities of material may be involved, losses due to incomplete solution, volatility, or adsorption must be avoided.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Glass filters*

Commercially available material, in size 203 by 254mm, is exhaustively washed prior to use.

5.4 *Cellulose filters*

Ashless, acid washed, analytical grade, in size 203 by 254mm.

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 *Nitric acid*

71%. Reagent grade.

5.8 *Standard solution of lead*

Dissolve 1.598g of lead nitrate and make up to 1 litre with 1% nitric acid. 1ml of this stock solution contains 1,000μg of lead, Pb.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

With meter, recorder or digital readout and monochromator with wavelength dial reading to 0.1 nanometre.

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

Graduated, Griffin form, with teflon coated rim, 150ml capacity.

6.7 *Hot plate*

Electric, with temperature control, thermostat and ceramic heating surface.

6.8 *Büchner funnel*

Polypropylene, custom made, with sintered false bottom and vacuum connection, 216 by 267 by 85mm in free depth.

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLE AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) are purified by placing a group of 100 such filters in the special Büchner funnel and extracting repetitively with distilled water. Mount the filter in a conventional high volume or other sampler head. Draw air through the filter at a flow rate between 1.13 and 1.60 cubic metres per minute, for an appropriate period, such as 24 hours. The resistance to flow offered by the cellulose filters is much greater than for glass and an appreciably smaller total volume of air will be taken with cellulose. Calculate and record the total volume of air sampled, in cubic metres, as the product of mean flow rate and time.

7.3 *Preparation of test sample*

Cut areal aliquots from the exposed surface of a filter using a circular metal punch. The cutting edge of the punch is carefully wiped with lens tissue between each use to prevent carry over of contamination from one sample to another. Place one or more such discs in a teflon beaker. Initiate the dissolution of the filter matrix by the dropwise addition of 1ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml volumetric flask and make up test sample to mark at 25°C. Mix the contents of the volumetric flask thoroughly after adjustment to volume. Transfer contents of volumetric flask to polyethylene storage bottle (6.4). The test sample is now ready for analysis. The above method applies to the digestion of glass fibre filters. Cellulose filters can be digested or extracted using nitric acid.

8. PROCEDURE

8.1 *Safety precautions*

Follow normal precautions for the handling of compressed gases. Observe manufacturer's instructions on lighting and extinguishing flame. TEST GAS SUPPLY SYSTEM FOR LEAKS BEFORE USE AND EACH TIME A CYLINDER OF GAS IS REPLACED.

8.2 *Test Portions*

8.2.1 Test portions, flame

Introduce the test portion into the flame by *continuous* aspiration, through polyethylene tubing, of an *unmeasured* portion of the test sample. Aspirate distilled water into flame, between the introduction of each test portion, to prevent cross contamination.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 *Calibration Curves*

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of lead by dilution of standard solution 5.8 to cover the range of 1.0 to 40.0 micrograms of lead per ml. Install in the monochromator and align, if necessary, the hollow cathode source for lead. Set the wavelength of the monochromator at 283.3nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard lead solution (8.2.1). At the same time, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of lead in micrograms per ml. Such a representative curve is given in Figure 1. Using the same dilute standard solutions of lead, and a distilled water blank, prepare a similar calibration curve with the wavelength of the monochromator set at 217.0nm. Representative curves, covering wavelengths 217.0 and 283.3nm, are given in Figure 2 (Page 11).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre portions of the dilute standard lead solutions and a distilled water blank in the furnace. Measure and record the response for each test portion following the predetermined measuring cycle. Cover the range 1 to 5 nanograms lead in steps of 1 nanogram (0.1 to 0.5 micrograms per ml for a 10 microlitre volume). Prepare a calibration curve of response, in arbitrary units, against concentration of lead in micrograms per ml. Such a representative curve is given in Figure 3 (Page 12).

8.4 *Determination*

8.4.1 Determination, flame

Set the wavelength of the monochromator at 283.3nm. Observing conditions of 8.2.1 and 8.3.1, aspirate an unmeasured portion of each test sample into the flame. Record the response for each unknown. Measure the lead in all the unknown test samples which can be accommodated to the calibration curve for 283.3nm. If greater sensitivity is required, this may be obtained by measuring at 217.0nm, at the cost of more electronic noise. If the lead content of a given test portion should be too low for both calibration curves, it will be necessary to use the flameless mode. If the lead content should prove to be too high for the 217.0nm curve it will then be necessary to dilute the test sample.

8.4.2 Determination, furnace

If insufficient sensitivity is available in the flame mode, measure into the furnace, by automatic pipette, a similar test portion of each unknown test sample. Follow the drying and heating programmes previously established. Record the response for each test portion in arbitrary units. If a test portion of 10 microlitres should provide insufficient response, repeat the measurement using larger test portions. Derive the amount of lead present, by referring to the appropriate calibration curve, Figure 3 (Page 12).

8.5 *Blank Tests*

8.5.1 Reagents

In parallel with preparation of calibration curves, prepare a reagent blank of the acids and distilled water used in the preparation of calibration curves and test samples. Change or purify reagents, as necessary, if blanks are unsatisfactory.

8.5.2 Reagents plus filters

In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 7.3. Measure lead and express blanks in micrograms of lead per ml.

9. EXPRESSION OF RESULTS

9.1 *Blanks*

The glass filter blank value for any element may vary considerably with the batch. This has been very noticeable with manganese and beryllium. For this reason, filter blanks should be determined regularly. It should also be noted that part of the filter blank value is due to matrix interferences from elements present in large amounts in the filter such as Na, Ba, Si, Ca, Zn, K and Al.

9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per ml. Typical precisions for ten repeat determinations on standard samples are: 15.00 ± 0.04μg/ml for the flame mode; 0.40 ± 0.0093μg/ml for the flameless mode, on a 10μl sample.

9.3 *Minimum measurable*

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.04 micrograms per ml in the case of lead, in the flame mode.

9.3.2 Concentration in air

This is based on a sample volume of 2,000 cubic metres, two aliquot discs 36mm in diameter and the use of the flame. This minimum measurable concentration is 0.010 micrograms of lead per cubic metre with glass and 0.0075 micrograms per cubic metre with cellulose.

9.4 *Calculations*

The lead content of the test portion is expressed in micrograms per ml, X_1. The blank, X_2, in the same units, is subtracted from X_1 to get the corrected concentration of lead in the test sample. Multiplication by the dilution factor, usually 25, gives the total quantity of lead in the test sample, in micrograms.

For high volume filters of nominal size 203 by 254mm:

Total exposed filter surface = 4.159×10^4 mm^2

Areal test portion, 2 x 36mm discs = 2,036mm^2

Surface multiplication factor = 20.43

Dilution factor = 25

Volume of air sampled, cubic metres = V

Response, unknown test portion = X_1

Response, total blank = X_2

Lead concentration, in $\mu g/m^3$ = T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 *Collection efficiencies*

Little is known about actual collection efficiencies, and these efficiencies are usually ignored in methods for the analysis of particulate metals. The particle size of particulate lead is below 1 micron according to Lee (12.2).

10.2 The effect of temperature and pressure during the sampling period has been largely disregarded in the past. Since these factors must have some effect on the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement that if standard conditions of temperature and pressure are to be used to correct the final volume, these conditions should be 25°C and 760mm Hg.

10.3 Although the method described is nominally based upon high volume samples taken for a 24-hour sampling period, there is no valid reason why samples may not be taken for shorter time periods, at slower flow rates, or both. If high volume samples are taken on cellulose, it is particularly appropriate to take air sample volumes of 1,000 cubic metres or less. The lower particulate loading, so obtained, minimizes particulate fall-off.

10.4 It is customary to assume that the decrease in air flow rate during sampling is linear and for usual purposes of calculation the mean value of initial and final flow rates is taken. This is not correct, although the error introduced by this oversimplification is not ordinarily serious.

10.5 For the preparation of areal test portions, the use of a sharp circular metal die is to be preferred over the use of scissors or rectilinear templates of large perimeter. Areal test portions prepared by these latter are less likely to be identical in size. A circular die, of limited diameter, machined from solid metal, is very rigid and areal aliquots can be very easily reproduced with accuracy. In the method described, a punch of stainless steel is used. No lead contamination has been found to result from its use.

10.6 In the repetitive and consecutive areal test portions cut from an exposed high volume filter, the assumption is implicit that the element of interest is uniformly distributed across the exposed surface of the filter.

This assumption is established as fact, at least in the case of lead and cadmium measured on high volume filters (12.3, 12.4, 12.5). This uniform distribution cannot be assumed in certain "membrane" type filters due to inherently high pressure drop and faulty geometry of commercially available filter holders. In the case of such filters, areal aliquotting cannot be used (12.6).

10.7 It is helpful, when it is possible, to have several calibration curves, relating to different sensitivities. This minimizes the possibility that the concentration of the metal in the unknown test sample will not match one or another of the curves. Thus, a certain sensitivity is available at 283.3nm, a higher sensitivity can be had at 217.0nm, and a still higher sensitivity by using the furnace. See Figures 1, 2 and 3 (Pages 11,12).

10.8 *Operating conditions, flame*

Wavelength = 282.3nm
Spectral band width = 0.7nm
Source = Hollow cathode
Source current = As recommended
Oxidant = Air
Fuel = Acetylene
Flame = Oxidizing, lean, blue
Sensitivity = 0.54μg/ml for 1% absorption

Change acetylene container before cylinder pressure drops below 50psig.

10.9 *Graphite furnace*

The calibration curve for the flame mode obeys Beer's Law up to and beyond 40 micrograms per ml for wavelength 283.3nm and up to 10 micrograms per ml for wavelength 217.0nm as shown in Figures 1 and 2. A representative curve for lead, measured by the graphite furnace, is given in Figure 3, which shows greatly increased sensitivity over the flame. Furnace operating conditions:

Wavelength = 283.3nm
Sample size = 10 microlitres
Purging gas = Argon or nitrogen
Thermal decomposition = drying (15sec, 100°C)
charring (15sec, 490°C)
atomizing (10sec, 2,400°C)

The use of a deuterium lamp background compensator is recommended.

11. SCHEMATIC REPRESENTATION OF PROCEDURE

11.1 Draw laboratory air sample.

11.2 Cut areal test portion from exposed filter surface.

11.3 Digest areal test portion.

11.4 Adjust digest to volume to give test sample.

11.5 Aspirate test portion into flame.

11.6 Or, add test portion to furnace.

12. REFERENCES

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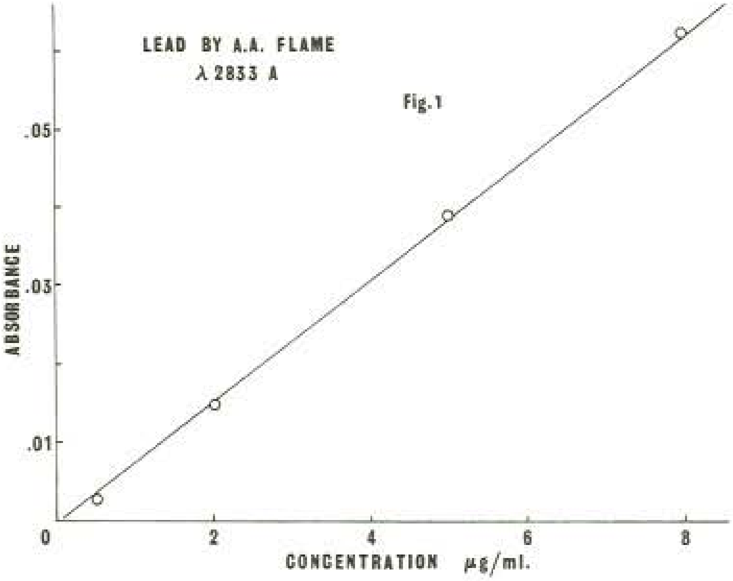


Fig. 1

LEAD BY A.A. FLAME
λ 2833 A
ABSORBANCE
.05
.03
.01
0
2
4
6
8
CONCENTRATION μg/ml.

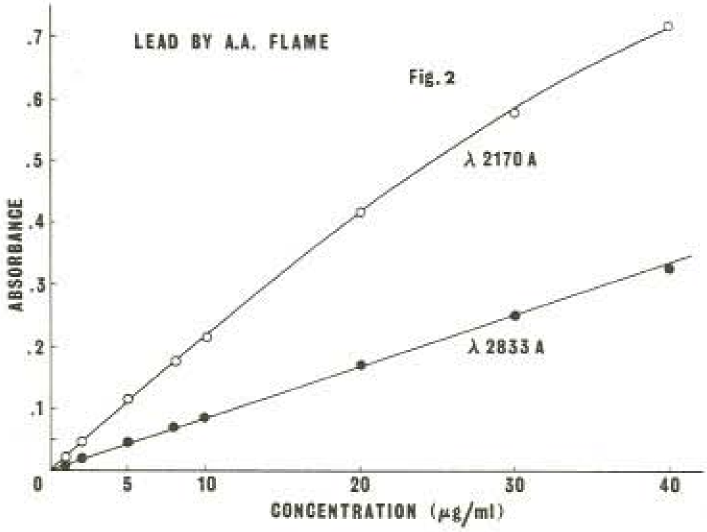
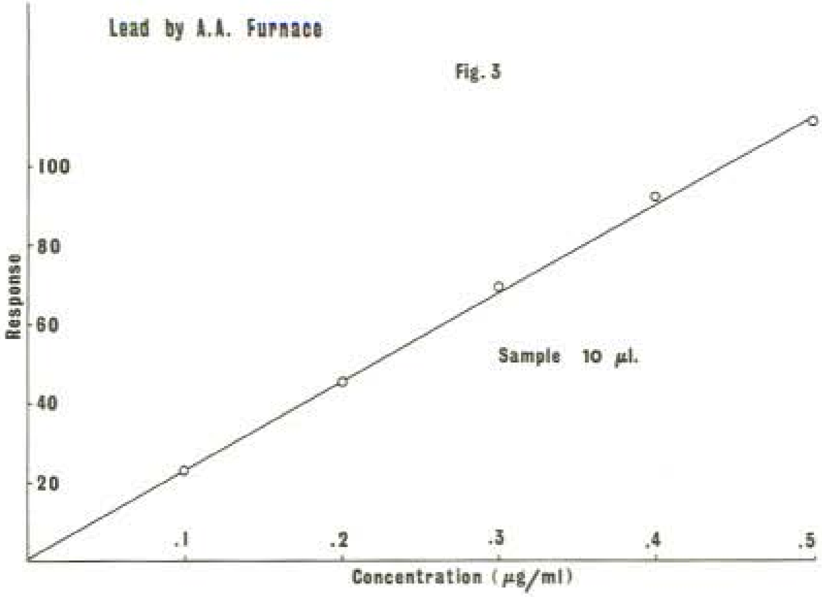


Fig. 2

LEAD BY A.A. FLAME
λ 2170 A
λ 2833 A
ABSORBANCE
.7
.6
.5
.4
.3
.2
.1
0
5
10
20
30
40
CONCENTRATION (μg/ml)



Lead by A.A. Furnace

Fig. 3