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Standard Reference Method for the Determination of Lead in Airborne Particulates (Atomic Absorption Spectrophotometry)

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Regulations, Codes, and Protocols
Report EPS 1-AP-75-4

Air Pollution
Control Directorate
February 1976

ENVIRONMENTAL PROTECTION SERVICE REPORT SERIES

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STANDARD REFERENCE METHOD FOR THE DETERMINATION OF LEAD IN AIRBORNE PARTICULATES (ATOMIC ABSORPTION SPECTROPHOTOMETRY)

Air Pollution Control Directorate

Environmental Protection Service

Report EPS 1-AP-75-4

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1 INTRODUCTION

In the method described, airborne particulates are collected by drawing 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 concentration of lead is calculated by reference to the appropriate calibration curve By using the flameless mode, additional sensitivity may be achieved beyond that of the usual flame The analytical results are expressed in micrograms per cubic metre of air. Details of accuracy and precision obtainable are given in section 9, "Expression of Results"

2 SCOPE AND FIELD OF APPLICATION

2.1 Applicability

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 vapour form, such as tetraethyl or tetramethyl lead, but may be readily adapted to the measurement of tetraethyl lead in gasoline

2.2 Measurement Range

Because airborne particulate lead may constitute 1% to 5% of airborne particulate matter, analytical sensitivity is not ordinarily a problem Based upon the flame mode, washed glass filters and a nominal air sample volume of 2000 m^3, lead is measurable to 0 010 $\mu g/m^3$ A slight improvement in sensitivity can be obtained by using cellulose filters (down to 0 0075 $\mu g/m^3$) For the same test sample, use of the flameless mode increases the sensitivity by at least a factor of 10.

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 lead 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 on line

5.2 Acetylene, Compressed. In pressure cylinders

5.3 Glass Filters. Commercially available material, 203 mm by 254 mm in size, is thoroughly washed prior to use

5.4 Cellulose Filters. Ashless, acid-washed, analytical grade, 203 mm by 254 mm in size

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 1 598 g of lead nitrate, and make up to one litre, with 1% nitric acid One millilitre of this stock solution contains 1000 μg of lead

6 APPARATUS

6.1 Spectrophotometer, Atomic Absorption. With meter, recorder or digital readout and monochromator with wavelength dial reading to 0 1 nm

6.2 Pipettes, Glass. Millilitre capacities, 'to deliver'

6.3 Volumetric Flasks. Borosilicate with ground glass stoppers, 25 ml capacity

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

6 5 Beakers, Teflon. Griffin form, 100 ml capacity

6.6 Beakers, Borosilicate. Graduated, Griffin form, with teflon-coated rim, 150 ml 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 mm by 267 mm by 85 mm in free depth

6.9 Graphite Furnace. One suitable instrument is available 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 of 10 μl to 100 μl

7 SAMPLING AND SAMPLES

7.1 Preparation of the Laboratory Sample

Cellulose filters (5 4) may be used without further treatment Glass fibre filters (5 3) are cleaned by placing a group of 100 such filters in the special Buchner 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 m^3/min and 1 60 m^3/min, for an appropriate period, such as 24 h Because the resistance to flow offered by the cellulose filters is much greater than that of glass, a smaller total volume of air may 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

7.2 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 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 1 ml 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 ml to 2 ml of nitric acid (5 7) and continue to heat gently until a few drops of nitric acid are left Add 10 ml of water, bring nearly to the boil and filter through a Whatman 41 filter into a glass beaker (6 6) Transfer to a 25-ml volumetric flask (6 3) Rinse the teflon beaker with another 10 ml of water, warm and filter into the same beaker Transfer to the 25-ml 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 the contents of the volumetric flask to a 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 FOR LEAKS BEFORE USE AND EACH TIME A CYLINDER OF GAS IS REPLACED.**

8.2 Treatment of Test Portions

8.2.1 Flame Method. 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 ***Furnace Method.*** Measure and insert in the furnace, test portions of 10 μl to 100 μl of the test sample using an automatic pipette (6 11)

8.3 Calibration Curves

8.3.1 ***Flame Method.*** Using 'to deliver' pipettes, prepare known concentrations of lead by dilution of standard solution (5 8) to cover the range of 1 0 μg to 40 0 μg lead/ml Install the hollow cathode source for lead in the spectrophotometer and align, if necessary Set the wavelength of the monochromator at 283 3 nm 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 versus concentration of lead in micrograms per millilitre A representative curve is shown 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 0 nm Representative curves, covering wavelengths 217 0 nm and 283 3 nm, are shown in Figure 2

8.3.2 ***Furnace Method.*** 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 The range of 1 ng to 5 ng of lead should be covered in steps of 1 ng (0 1 μg/ml to 0 5 μg/ml for a 10 μl volume) Prepare a calibration curve of response, in arbitrary units, versus concentration of lead in micrograms per millilitre A typical response curve is shown in Figure 3

8.4 Lead Determination

8.4.1 ***Flame Method.*** Set the wavelength of the monochromator at 283 3 nm Observing the 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 3 nm If greater sensitivity is required, this may be obtained by measuring at 217 0 nm, at the cost of more electronic noise If the lead content of a given test portion is too low for both calibration curves, it will be necessary to use the flameless mode If the lead content is too high for the 217 0 nm curve it will then be necessary to dilute the test sample

8.4.2 ***Furnace Method.*** If the sensitivity of the flame mode is insufficient, measure into the furnace, by automatic pipette, a similar test portion of each unknown test sample Follow the drying and heating programs previously established Record the response for each test portion in arbitrary units If a test portion of 10 μl should provide insufficient response, repeat the measurement using larger test portions Determine the amount of lead present, by referring to the appropriate calibration curve (e g , Figure 3)

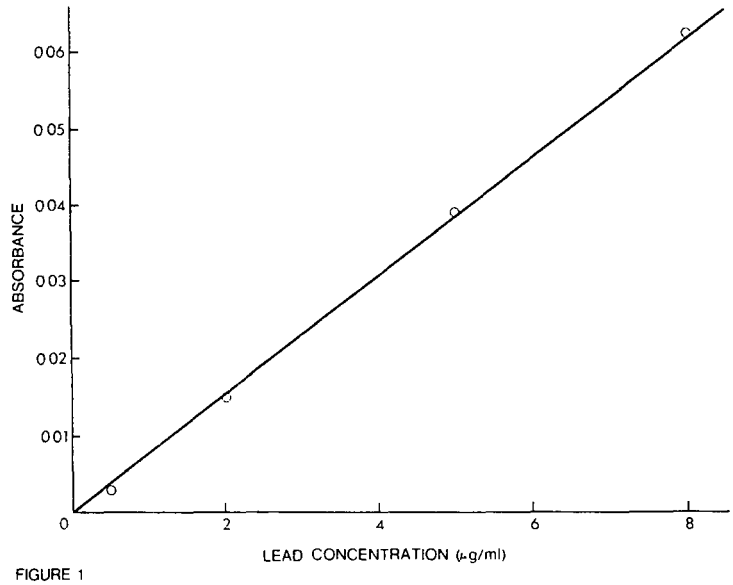

FIGURE 1

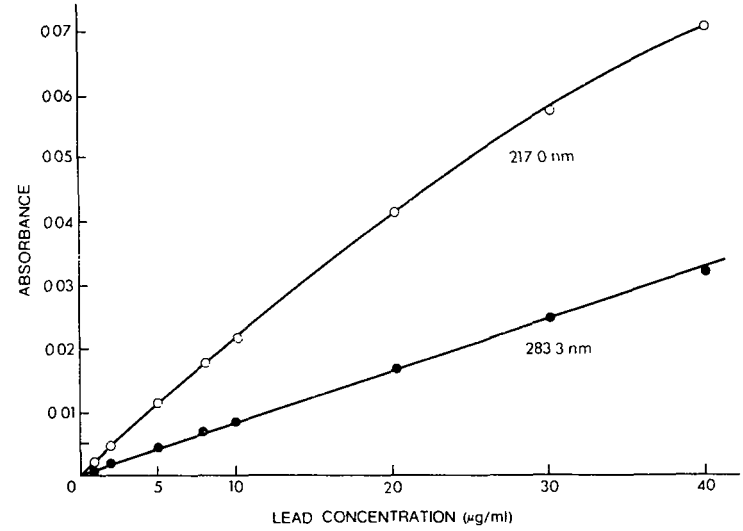

FIGURE 2

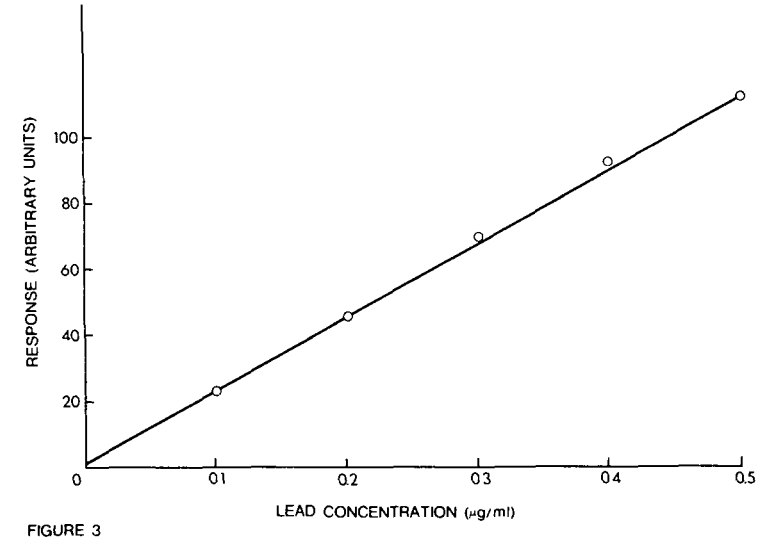

FIGURE 3

8.5 Blank Tests

8.5.1 ***Reagents.*** While preparing 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.*** While preparing calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 7.2 Measure lead and express blanks in micrograms of lead per millilitre.

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 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 millilitre Typical precisions for ten repeat determinations on standard samples are 15 00 ± 0 04 μg/ml for the flame mode, 0 4000 ± 0.0093 μg/ml for the flameless mode, on a 10 μl 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 μg/ml in the case of lead, in the flame mode.

9.3.2 ***Concentration in Air.*** This is based on a sample volume of 2000 m^3, two aliquot discs 36 mm in diameter, and the use of the flame This minimum measurable concentration is 0 010 μg lead/m^3 with glass and 0.0075 $\mu g/m^3$ with cellulose

9.4 Calculations

The lead content of the test portion is expressed in micrograms per millilitre, 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 mm x 254 mm

Total exposed filter surface	4.159×10^4 mm^2
Areal test portion, 2mm x 36 mm discs	2036 mm^2
Surface multiplication factor	20.43

Dilution factor	25
Volume of air sampled, m^3	V
Response, unknown test portion	X_1
Response, total blank	X_2
Lead concentration, $\mu g/m^3$	T

$$T = \frac{(X_1 - X_2) \times 20\ 43 \times 25}{V}$$

10 NOTES ON PROCEDURE

10.1 Collection Efficiency

Recent work suggests that for 24-h, high-volume sampling, particulate collection is equivalent on unwashed glass fibre filters, MSA 1106B, as compared with analytical grade cellulose Whatman 41 (1) According to Lee, the mass median diameter of airborne particulate lead is below 1 μm (2) There is some evidence that more lead is collected when the particular filter porosity is minimal (3) There is also evidence that collection efficiency decreases as face velocity increases (3,4) Maximum collection efficiencies can be expected with low face velocities and low-volume air sampling (4)

10.2 Blanks

In general, washed or unwashed high-volume filters of glass fibre are not satisfactory for trace metal analysis because of the overwhelming blanks In the single case of lead, however, the 24-h collection of particulate lead in most urban and industrial environments is so enormous that the lead blank of the filter makes no noticeable difference to the accuracy of the analytical result, regardless of whether analytical cellulose, unwashed glass or washed glass is used(5,6) When monitoring of the trends during a 24-h period is required, all due care is necessary to use filter media with the lowest possible lead blank Noller and Bloom found that it was necessary to acid wash Millipore filter material before use in order to reduce the significant lead blank (7)

10.3 Distribution

In the analysis of the consecutive and 'replicate' areal test portions cut from a high volume filter, the assumption is implicit that the element is uniformly distributed across the exposed surface of the filter This assumption has been established as fact, at least in the case of particulate lead collected on high-volume filters (6,8) This uniform distribution cannot be assumed for certain 'membrane-type' filters where uneven distribution has been found In the case of such filters, areal aliquotting cannot be used (9)

10.4 Areal Test Portions

For the preparation of areal test portions, the use of a sharp circular metal die is preferred over scissors or adjustable templates for reasons of reproducibility A circular metal die, machined from solid stock, is very rigid and areal aliquots are easily reproduced In the method described, a punch of stainless steel is used. No lead contamination has been found to result from its use

10.5 Sampling Time

Although the method described is nominally based upon high-volume samples taken for a 24-h sampling period, there is no reason why samples may not be taken for shorter time periods and at slower flow rates (7) If high-volume samples are taken on cellulose, it may be desirable to take an air sample volume of 1000 m^3 or less, as the smaller quantity of particulates so collected will have less tendency to fall off

10.6 Air Flow Rate

It is customary to assume, in high-volume sampling, that the decrease in air flow rate 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 For low-volume samples of 200 cm^3, containing 0 2 ng of lead, the volume must be accurately known (7)

10.7 Effect of Temperature and Pressure

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 This is particularly important with the increasing use of smaller air sample volumes (7) There is general agreement that if standard conditions of temperature and pressure are to be used to correct the measured volume, these conditions should be 25°C and 760 mm Hg

10.8 Calibration Curves

It is helpful, when possible, to have several calibration curves relating to different sensitivities This minimizes the possibility that the concentration of lead in the unknown test sample will not match one or another of the curves Thus, a certain sensitivity is available at 283 3 nm, a higher sensitivity at 217 0 nm, and a still higher sensitivity can be obtained using the flameless mode (see Figures 1, 2 and 3)

10.9 Operating Conditions, Flame

Wavelength	283 3 nm
Spectral band width	0 7 nm

Source	hollow cathode
Source current	as recommended
Oxidant	air
Fuel	acetylene
Flame	oxidizing, lean, blue
Sensitivity	0 54 g/ml for 1% absorption

CHANGE ACETYLENE CONTAINER BEFORE CYLINDER PRESSURE DROPS BELOW 50 PSIG.

10.10 Graphite Furnace

A representative curve for lead, measured by the graphite furnace, is given in Figure 3, which shows greatly increased sensitivity over the flame, (illustrated in Figures 1 and 2)

Furnace operating conditions

Wavelength		283 3 nm
Sample size		10 0 μl
Purging gas		argon or nitrogen
Thermal decomposition	(drying	15 s, 100°C
	(charring	15 s, 490°C
	(atomizing	10 s, 2400°C

The use of a deuterium lamp background compensator is recommended

11 SCHEMATIC REPRESENTATION OF PROCEDURE

11.1 Draw air sample

11.2 Cut areal test portion, alternatively, use entire filter

11.3 Digest areal test portion (or filter)

11.4 Adjust digest to volume to give test sample

11.5 Aspirate test portion into flame

11.6 Or, insert 10-μl aliquot of test portion in furnace

REFERENCES

1 Neustadter, H E , Sidik, S M , King, R B , Fordyce, J A and Burr, J C "The Use of Whatman 41 Filters for High Volume Sampling", *Atmos. Environment, 9,* 101 (1975)

2 Lee, R E , Patterson, R K , Creder, W L and Wagman, J "Concentration and Particle Size Distribution of Particulate Emissions in Automobile Exhaust", *Atmos. Environment, 5,* 225 (1971)

3 Seeley, J L and Skogerboe, R K "Combined Sampling Analysis Method for the Determination of Lead Elements in Atmospheric Particulates", *Anal Chem., 46,* 415 (1974)

4 Cohen, S L "Dependence of Hi-Vol Measurements on Flow Rate", *Environ Sci. Technol., 7,* 60 (1973)

5 Sumi, L , Corkery, A and Monkman, J L "Calcium Sulphate Content of Urban Air", *Geophysical Monograph, 3,* 69 (1959)

6 Zdrojewski, A , Quickert, N , Dubois, L and Monkman, J L "The Accurate Measurement of Lead in Airborne Particulates", *Int. J. Environ Anal Chem., 2,* 63 (1972)

7 Noller, B N and Bloom, H "The Determination of Atmospheric Particulate Lead Using Low Volume Sampling and Non-Flame Atomic Absorption", *Atmos. Environment, 9,* 505 (1975)

8 Dubois, L , Teichman, T , Airth, J M and Monkman, J L "The Metal Content of Urban Air", *Journal Air Poll Control Assoc., 16,* 77 (1966)

9 Pierce, J O and Meyer, J H "Sampling and Analysis Considerations in Evaluating Levels of Atmospheric Lead", *Atmos Environment, 5,* 811 (1971)