⬥EPA

Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air and Proposed Equivalency Regulations

REFERENCE METHOD FOR THE DETERMINATION OF LEAD IN

SUSPENDED PARTICULATE MATTER COLLECTED FROM AMBIENT AIR

1. Principle and Applicability

    1.1   Ambient air suspended particulate matter is collected on a glass-fiber filter for 24-hours using a high volume air sampler.

    1.2   Lead in the particulate matter is solubilized by extraction with nitric acid (HNO_3), facilitated by heat or by a mixture of HNO_3 and hydrochloric acid (HCl) facilitated by ultrasonication.

    1.3   The lead content of the sample is analyzed by atomic absorption spectrometry using an air-acetylene flame, the 283.3 or 217.0 nm lead absorption line, and the optimum instrumental conditions recommended by the manufacturer.

    1.4   The ultrasonication extraction with HNO_3/HCl will extract metals other than lead from ambient particulate matter.

2. Range, Sensitivity and Lower Detectable Limit

    The values given below are typical of the methods capabilities. Absolute values will vary for individual situations depending on the type of instrument used, the lead line, and operating conditions.

    2.1   Range. The typical range of the method is 0.07 to 7.5 μg Pb/m^3 assuming an upper linear range of analysis of 15 $\mu g/ml$ and an air volume of 2400 m^3.

    2.2   Sensitivity. Typical sensitivities for a 1% change in absorption (0.0044 absorbance units) are 0.2 and 0.5 μg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

2.3   Lower Detectable Limit (LDL). A typical LDL is 0.07 µg Pb/m^3. The above value was calculated by doubling the between-laboratory standard deviation obtained for the lowest measurable lead concentration in a collaborative test of the method.[15] An air volume of 2400 m^3 was assumed.

3. Interferences

Two types of interferences are possible: chemical, and light scattering.

3.1   Chemical. Reports on the absence [1,2,3,4,5] of chemical interferences far outweigh those reporting their presence,[6] therefore, no correction for chemical interferences is given here. If the analyst suspects that the sample matrix is causing a chemical interference, the interference can be verified and corrected for by carrying out the analysis with and without the method of standard additions.[7]

3.2   Light Scattering. Non-atomic absorption or light scattering, produced by high concentrations of dissolved solids in the sample, can produce a significant interference, especially at low lead concentrations.[2] The interference is greater at the 217.0 nm line than at the 283.3 nm line. No interference was observed using the 283.3 nm line with a similar method.[1]

Light scattering interferences can, however, be corrected for instrumentally. Since the dissolved solids can vary depending on the origin of the sample, the correction may be necessary, especially when using the 217.0 nm line. Dual beam instruments with a continuum source give the most accurate correction. A less accurate correction can be obtained by using a non-absorbing lead line that is near the lead analytical line. Information on use of these correction techniques can be obtained from instrument manufacturers' manuals.

If instrumental correction is not feasible, the interference can be eliminated by use of the ammonium pyrrolidinecarbodithioate-methylisobutyl ketone, chelation-solvent extraction technique of sample preparation.[8]

4. Precision and Bias

4.1 The high-volume sampling procedure used to collect ambient air particulate matter has a between-laboratory relative standard deviation of 3.7% over the range 80 to 125 $\mu g/m^3$.[9] The combined extraction - analysis procedure has an average within-laboratory relative standard deviation of 5 to 6% over the range 1.5 to 15 μg Pb/ml, and an average between laboratory relative standard deviation of 7 to 9% over the same range. These values include use of either extraction procedure.

4.2 Single laboratory experiments and collaborative testing indicate that there is no significant difference in lead recovery between the hot and ultrasonic extraction procedures.[15]

5. Apparatus

5.1 Sampling.

5.1.1   High-volume sampler. Use and calibrate the sampler as described in reference 10.

5.2 Analysis.

5.2.1   Atomic Absorption Spectrophotometer. Equipped with lead hollow cathode or electrodeless discharge lamp.

5.2.1.1 Acetylene. The grade recommended by the instrument manufacturer should be used. Change cylinder when pressure drops below 50-100 psig.

5.2.1.2 Air. Filtered to remove particulate, oil and water.

5.2.2   Glassware. Class A borosilicate glassware should be used throughout the analysis.

5.2.2.1   Beakers. 30 and 150 ml. graduated, Pyrex.

5.2.2.2   Volumetric flasks. 100-ml.

5.2.2.3   Pipettes. To deliver 50, 30, 15, 8, 4, 2, 1 ml.

5.2.2.4   Cleaning. All glassware should be scrupulously cleaned. The following procedure is suggested. Wash with laboratory detergent, rinse, soak for 4 hours in 20% (w/w) HNO_3, rinse 3 times with distilled-deionized water, and dry in a dust free manner.

5.2.3   Hot plate.

5.2.4   Ultrasonication water bath, unheated. Commercially available laboratory ultrasonic cleaning baths of 450 watts or higher "cleaning power", i.e., actual ultrasonic power output to the bath have been found satisfactory.

5.2.5   Template. To aid in sectioning the glass-fiber filter. See Figure 1 for dimensions.

5.2.6   Pizza cutter. Thin wheel. Thickness <1 mm.

5.2.7   Watch glass.

5.2.8   Polyethylene bottles. For storage of samples. Linear polyethylene gives better storage stability than other polyethylenes and is preferred.

5.2.9   Parafilm "M".* American Can Company, Marathon Products, Nennah, Wisconsin, or equivalent.

6.   Reagents

6.1   Sampling

6.1.1   Glass fiber filters. The specifications given below are intended to aid the user in obtaining high quality filters with reproducible properties. These specifications have been met by EPA contractors.

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*Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

6.1.1.1   Lead content. The absolute lead content of filters is not critical, but low values are, of course, desirable. EPA typically obtains filters with a lead content of <75 µg/filter.

It is important that the variation in lead content from filter to filter, within a given batch, be small.

6.1.1.2   Testing.

6.1.1.2.1   For large batches of filters (> 500 filters) select at random 20 to 30 filters from a given batch. For small batches (< 500 filters) a lesser number of filters may be taken. Cut one 3/4" x 8" strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in Sections 7 and 8.

6.1.1.2.2   Calculate the total lead in each filter as

$$F_b = µg \ Pb/ml \times \frac{100 \ ml}{strip} \times \frac{12 \ strips}{filter}$$

where:

F_b = Amount of lead per 72 square inches of filter, µg.

6.1.1.2.3   Calculate the mean, $\overline{F}_b$, of the values and the relative standard deviation (standard deviation/mean x 100). If the relative standard deviation is high enough so that, in the analysts opinion, subtraction of $\overline{F}_b$, (Section 10.3) may result in a significant error in the µg Pb/m^3, the batch should be rejected.

6.1.1.2.4   For acceptable batches, use the value of $\overline{F}_b$ to correct all lead analyses (Section 10.3) of particulate matter collected using that batch of filters. If the analyses are below the LDL (Section 2.3) no correction is necessary.

6.2   Analysis

6.2.1   Concentrated (15.6 M) HNO_3. ACS reagent grade HNO_3 and commercially available redistilled HNO_3 has been found to have sufficiently low lead concentrations.

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6.2.2   Concentrated (11.7 $\underline{M}$) HCl. ACS reagent grade.

6.2.3   Distilled-deionized water. (D.I. water).

6.2.4   3 $\underline{M}$ HNO_3. This solution is used in the hot extraction procedure. To prepare, add 192 ml of concentrated HNO_3 to D.I. water in a 1 ℓ volumetric flask. Shake well, cool, and dilute to volume with D.I. water. CAUTION: Nitric Acid Fumes Are Toxic. Prepare in a well ventilated fume hood.

6.2.5   0.45 $\underline{M}$ HNO_3. This solution is used as the matrix for calibration standards when using the hot extraction procedure. To prepare, add 29 ml of concentrated HNO_3 to D.I. water in a 1 ℓ volumetric flask. Shake well, cool, and dilute to volume with D.I. water.

6.2.6   2.6 $\underline{M}$ HNO_3 + 0 to 0.9 $\underline{M}$ HCl. This solution is used in the ultrasonic extraction procedure. The concentration of HCl can be varied from 0 to 0.9 $\underline{M}$. Directions are given for preparation of a 2.6 $\underline{M}$ HNO_3 + 0.9 $\underline{M}$ HCl solution. Place 167 ml of concentrated HNO_3 into a 1ℓ volumetric flask and add 77 ml of concentrated HCl. Stir 4 to 6 hours, dilute to nearly 1 ℓ with D.I. water, cool to room temperature, and dilute to 1ℓ.

6.2.7   0.40 $\underline{M}$ HNO_3 + X $\underline{M}$ HCl. This solution is used as the matrix for calibration standards when using the ultrasonic extraction procedure. To prepare, add 26 ml of concentrated HNO_3, plus the ml of HCl required, to a 1ℓ volumetric flask. Dilute to nearly 1ℓ with D.I. water, cool to room temperature, and dilute to 1ℓ. The amount of HCl required can be determined from the following equation:

$$y = \frac{77 \text{ ml} \times 0.15 \text{ } x}{0.9 \text{ M}}$$

where:

   y = ml of concentrated HCl required

   x = molarity of HCl in 6.2.6

   0.15 = dilution factor in 7.2.2

6.2.8   Lead Nitrate, $Pb(NO_3)_2$. ACS reagent grade, purity 99.0%. Heat for 4-hours at 120°C and cool in a desiccator.

6.3   Calibration Standards

6.3.1   Master standard, 1000 μg Pb/ml in HNO_3. Dissolve 1.598 g of $Pb(NO_3)_2$ in 0.45 $\underline{M}$ HNO_3 contained in a 1 ι volumetric flask and dilute to volume with 0.45 $\underline{M}$ HNO_3.

6.3.2   Master Standard, 1000 μg Pb/ml in HNO_3/HCl. Prepare as in 6.3.1 except use the HNO_3/HCl solution in 6.2.7.

Store standards in a polyethylene bottle. Commercially available certified lead standard solutions may also be used.

7. Procedure

7.1   Sampling. Collect samples for 24-hours using the procedure described in reference 10 with glass-fiber filters meeting the specifications in 6.1.1. Transport collected samples to the laboratory taking care to minimize contamination and loss of sample.[17]

7.2   Sample Preparation.

7.2.1   Hot Extraction Procedure

7.2.1.1   Cut a 3/4" x 8" strip from the exposed filter using a template and a pizza cutter as described in Figures 1 and 2. Other cutting procedures may be used.

Lead in ambient particulate matter collected on glass fiber filters has been shown to be uniformly distributed across the filter [1,3,11] suggesting that the position of the strip is unimportant. However, another study[12] has shown that when sampling near a road-way lead is not uniformly distributed acros the filter. The nonuniformity has been attributed to large variations in particle size.[16] Therefore, when sampling near a road-way, additional strips at different positions within the filter should be analyzed.

7.2.1.2   Fold the strip in half twice and place in a 150-ml beaker. Add 15 ml of 3 $\underline{M}$ HNO_3 to cover the sample. The acid should completely cover the sample Cover the beaker with a watch glass.

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7.2.1.3   Place beaker on the hot-plate, contained in a fume hood, and boil gently for 30 min. Do not let the sample evaporate to dryness. CAUTION: Nitric Acid Fumes Are Toxic.

7.2.1.4   Remove beaker from hot plate and cool to near room temperature.

7.2.1.5   Quantitatively transfer the sample as follows:

7.2.1.5.1   Rinse watch glass and sides of beaker with D.I. water.

7.2.1.5.2   Decant extract and rinsings into a 100-ml volumetric flask.

7.2.1.5.3   Add D.I. water to 40 ml mark on beaker, cover with watch glass, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted since it allows the HNO_3 trapped in the filter to diffuse into the rinse water.

7.2.1.5.4   Decant the water from the filter into the volumetric flask.

7.2.1.5.5   Rinse filter and beaker twice with D.I. water and add rinsings to volumetric flask until total volume is 80 to 85 ml.

7.2.1.5.6   Stopper flask and shake vigorously. Set aside for approximately 5 minutes or until foam has dissipated.

7.2.1.5.7   Bring solution to volume with D.I. water. Mix thoroughly.

7.2.1.5.8   Allow solution to settle for one hour before proceeding with analysis.

7.2.1.5.9   If sample is to be stored for subsequent analysis, transfer to a linear polyethylene bottle.

7.2.2   Ultrasonic Extraction Procedure

7.2.2.1   Cut a 3/4" x 8" strip from the exposed filter as described in Section 7.2.1.1.

7.2.2.2   Fold the strip in half twice and place in a 30 ml beaker. Add 15 ml of the HNO_3/HCl solution in 6.2.6. The acid should completely cover the sample. Cover the beaker with Parafilm.

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The Parafilm should be placed over the beaker such that none of the Parafilm is in contact with water in the ultrasonic bath. Otherwise, rinsing of the Parafilm (Section 7.2.2.4.1) may contaminate the sample.

7.2.2.3   Place the beaker in the ultrasonication bath and operate for 30 minutes.

7.2.2.4   Quantitatively transfer the sample as follows:

7.2.2.4.1   Rinse Parafilm and sides of beaker with D.I. water.

7.2.2.4.2   Decant extract and rinsings into a 100 ml volumetric flask.

7.2.2.4.3   Add 20 ml D.I. water to cover the filter strip, cover with parafilm, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted. The sample is then processed as in Sections 7.2.1.5.4 through 7.2.1.5.9. NOTE: Samples prepared by the hot extraction procedure are now in 0.45 $\underline{M}$ HNO_3. Samples prepared by the ultrasonication procedure are in 0.40 $\underline{M}$ HNO_3 + X $\underline{M}HCl$.

8.   Analysis

8.1   Set the wavelength of the monochromator at 283.3 or 217.0 nm. Set or align other instrumental operating conditions as recommended by the manufacturer.

8.2   The sample can be analyzed directly from the volumetric flask, or an appropriate amount of sample decanted into a sample analysis tube. In either case, care should be taken not to disturb the settled solids.

8.3   Aspirate samples, calibration standards and blanks (Section 9.2) into the flame and record the equilibrium absorbance.

8.4   Determine the lead concentration in ug Pb/ml, from the calibration curve, Section 9.3.

8.5   Samples that exceed the linear calibration range should be diluted with acid of the same concentration as the calibration standards and reanalyzed.

9. Calibration

9.1   Working Standard, 20 µg Pb/ml. Prepared by diluting 2.0 ml of the master standard (6.3.1 if the hot acid extraction was used or 6.3.2 if the ultrasonic extraction procedure was used) to 100 ml with acid of the same concentration as used in preparing the master standard.

9.2   Calibration standards. Prepare daily by diluting the working standard, with the same acid matrix, as indicated below. Other lead concentrations may be used.

Volume of 20 µg/ml Working Standard, ml	Final Volume, ml	Concentration µg Pb/ml
0	100	0.0
1.0	200	0.1
2.0	200	0.2
2.0	100	0.4
4.0	100	0.8
8.0	100	1.6
15.0	100	3.0
30.0	100	6.0
50.0	100	10.0
100	100	20.0

9.3   Preparation of calibration curve. Since the working range of analysis will vary depending on which lead line is used and the type of instrument, no one set of instructions for preparation of a calibration curve can be given. Select standards (plus the reagent blank), in the same acid concentration as the samples, to cover the linear absorption range indicated by the instrument manufacturer. Measure the absorbance of the blank and standards as in Section 8.0. Repeat until good agreement is obtained between replicates. Plot absorbance

(y-axis) versus concentration in µg Pb/ml (x-axis). Draw (or compute) a straight line through the linear portion of the curve. Do not force the calibration curve through zero. Other calibration procedures may be used.

To determine stability of the calibration curve, remeasure - alternately - one of the following calibration standards for every 10th sample analyzed: concentration $\leq$ 1 µg Pb/ml; concentration $\leq$ 10 µg Pb/ml. If either standard deviates by more than 5% from the value predicted by the calibration curve, recalibrate and repeat the previous 10 analyses.

10. Calculation.

10.1   Measured air volume. Calculate the measured air volume as

$$V_m = \frac{Q_i + Q_f}{2} \times T$$

where:

V_m = Air volume sampled (uncorrected), m^3

Q_i = Initial air flow rate, m^3/min.

Q_f = Final air flow rate, m^3/min.

T = Sampling Time, min.

The flow rates Q_i and Q_f should be corrected to the temperature and pressure conditions existing at the time of orifice calibration as directed in addendum B of reference 10, before calculation of V_m.

10.2 Air volume at STP. The measured air volume is corrected to reference conditions of 760 mm Hg and 25°C as follows. The units are standard cubic meters, sm^3.

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V_m = Measured volume from 10.1

P_2 = Atmospheric pressure at time of orifice calibration, mm Hg

P_1 = 760 mm Hg

T_2 = Atmospheric temperature at time of orifice calibration, °K

T_1 = 298°K

10.3   Lead Concentration. Calculate lead concentration in the air sample.

$$C = \frac{(\mu g\ Pb/ml \times 100\ ml/strip \times 12\ strips/filter) - \overline{F}_b}{V_{STP}}$$

where:

C = Concentration, $\mu g\ Pb/sm^3$

$\mu g\ Pb/ml$ = Lead concentration determined from Section 8

100 ml/strip = Total sample volume

12 strips/filter = $\dfrac{\text{Useable filter area, 7" x 9"}}{\text{Exposed area of one strip, 3/4" x 7"}}$

$\overline{F}_b$ = Lead concentration of blank filter, μg, from Section 6.1.1.2.3

V_{STP} = Air volume from 10. 2

11. Quality Control

3/4" x 8" glass fiber filter strips containing 80 to 2000 μg Pb/strip (as lead salts) and blank strips with zero Pb content should be used to

determine if the method - as being used - has any bias. Quality control charts should be established to monitor differences between measured and true values. The frequency of such checks will depend on the local quality control program.

To minimize the possibility of generating unreliable data, the user should follow practices established for assuring the quality of air pollution data,[13] and take part in EPA's semi-annual audit program for lead analyses.

12. Trouble Shooting

1.   During extraction of lead by the hot extraction procedure, it is important to keep the sample covered so that corrosion products - formed on fume hood surfaces which may contain lead - are not deposited in the extract.

2.   The sample acid concentration should minimize corrosion of the nebulizer. However, different nebulizers may require lower acid concentrations. Lower concentrations can be used provided samples and standards have the same acid concentration.

3.   Ashing of particulate samples has been found, by EPA and contractor laboratories, to be unnecessary in lead analyses by Atomic Absorption. Therefore, this step was omitted from the method.

4.   Filtration of extracted samples, to remove particulate matter, was specifically excluded from sample preparation, because some analysts have observed losses of lead due to filtration.

5.   If suspended solids should clog the neublizer during analysis of samples, centrifuge the sample to remove the solids.

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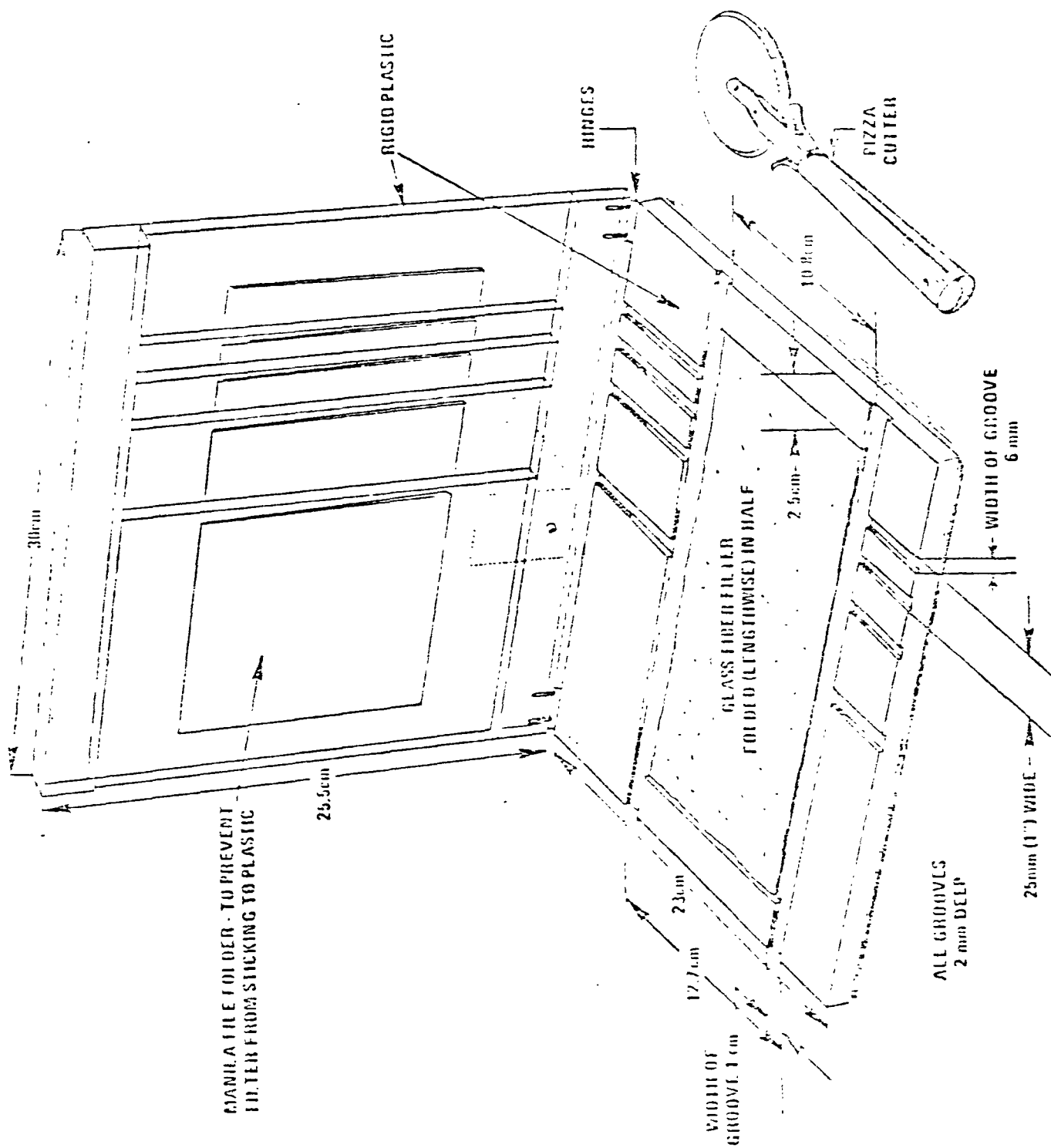
RIGID PLASTIC

HINGES

PIZZA CUTTER

10.8cm

30cm

MANILA FILE FOLDER - TO PREVENT
FILTER FROM STICKING TO PLASTIC

25.5cm

GLASS FIBER FILTER
FOLDED (LENGTHWISE) IN HALF

2.5cm

WIDTH OF GROOVE
6 mm

23cm

12.7cm

ALL GROOVES
2 mm DEEP

WIDTH OF
GROOVE 1cm

25mm (1") WIDE

Figure 1

Apparatus and Procedure For Cutting Glass Fiber Filter Strips

19mm (¾")

1mm SLIT

¾" x 8" STRIP FOR
LEAD ANALYSIS

STRIPS FOR
OTHER ANALYSES

Figure 2
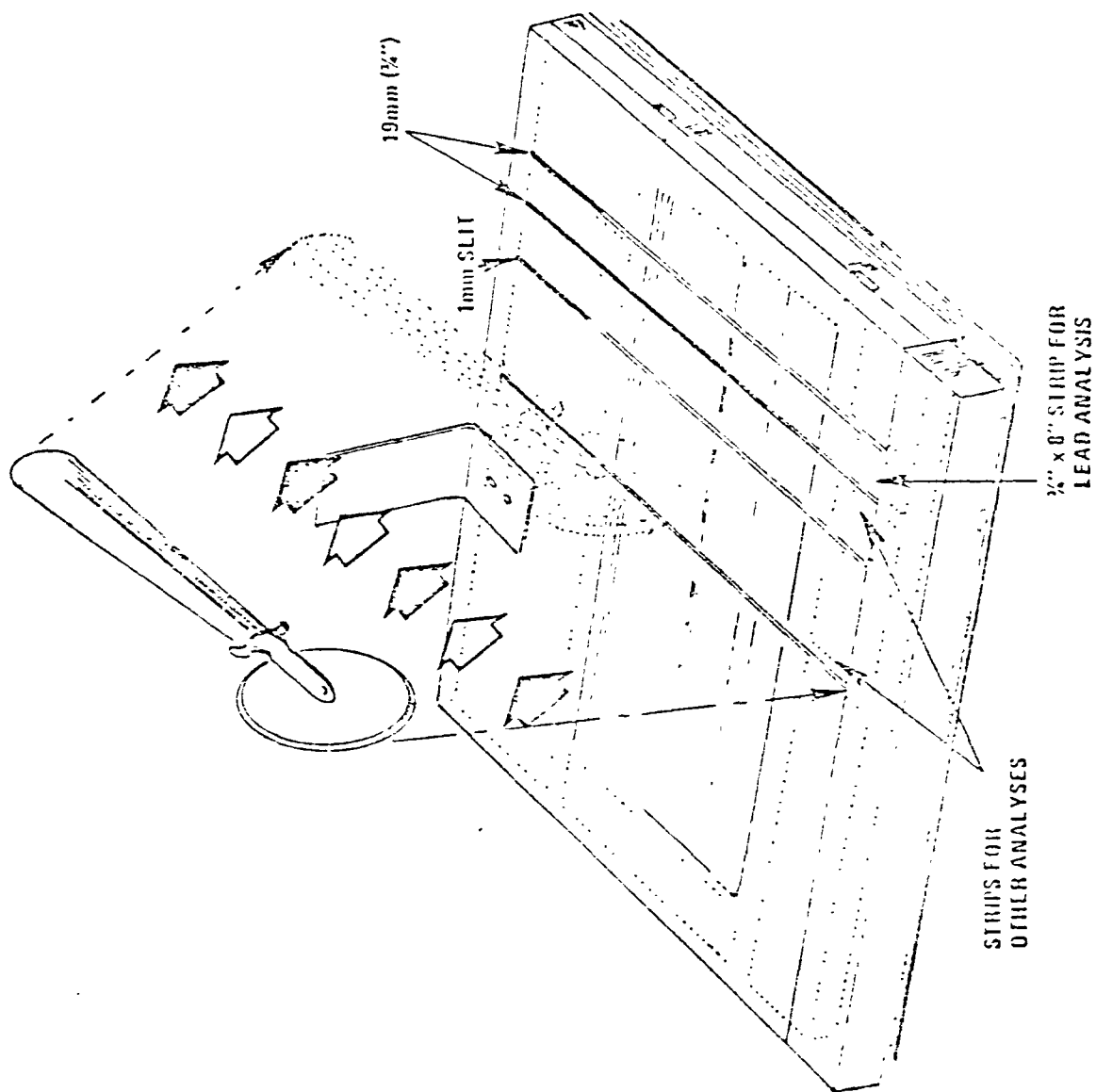
Apparatus and Procedure for Cutting Glass Fiber Filter Strips

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Parts 51 and 53]

AMBIENT AIR MONITORING REFERENCE AND

EQUIVALENT METHODS FOR LEAD

Notice of Proposed Rulemaking

AGENCY: Environmental Protection Agency (EPA)

ACTION: Proposed rulemaking

SUMMARY: On December 14, 1977, new national primary and secon-

dary ambient air quality standards for lead were proposed (42FR

63076).   Atmospheric lead is proposed to be measured as elemental

lead, either by the proposed reference method or "by an equiva-

lent method."   The amendments proposed below would provide the

necessary and appropriate changes in the existing equivalent

method regulations (primarily contained in 40 CFR Part 53) to

allow the designation of equivalent methods for measuring atmos-

pheric lead concentrations.

DATES: Comments relative to these proposed regulations must be

received by [45 days after publication in the Federal Register].

ADDRESS: Send comments to: Mr. Larry J. Purdue
                               Department E (MD-76)
                               Environmental Monitoring and Support
                               Laboratory

U.S. Environmental Protection
Agency
Research Triangle Park, N.C.   27711

FOR FURTHER INFORMATION CONTACT: Mr. Larry Purdue, Telephone

919/541-3076 (FTS 629-3076).

INCIDENTAL INFORMATION: The proposed reference method for mea-

suring atmospheric lead, as well as much associated information,

was published in the December 14, 1977 issue of the Federal

Register (Volume 42), starting on page 63076.

SUPPLEMENTARY INFORMATION:

Background

When the first National Ambient Air Quality Standards were

promulgated in 1971 (36 FR 8186, April 30, 1971), EPA established

the concept that measurements of ambient air pollutants used to

determine compliance with the standards must be made with either

a specified "reference method" or with an alternate method which

could be shown to be "equivalent" to the reference method. The

air quality standards are now contained in Part 50 of Title 40 of

the Code of Federal Regulations (40 CFR Part 50). Appendixes to

Part 50 specify either a prescribed reference method, or a measure-

ment principle and calibration procedure applicable to reference

methods, for each pollutant for which a standard has been promulgated.

On February 18, 1975, EPA promulgated regulations to establish definitive requirements and procedures by which methods for measuring specified air pollutants may be designated "reference methods" or "equivalent methods" (40 FR 7044, February 18, 1975). These regulations are contained in 40 CFR Part 53. Originally these "equivalency" regulations were applicable only to methods for measuring SO_2, CO, and photochemical oxidants (O_3), but were subsequently amended to cover methods for NO_2 as well (41 FR 52692, December 1, 1976).

On December 14, 1977, EPA proposed amendments to 40 CFR Part 50 to establish new National Primary and Secondary Ambient Air Quality Standards for lead. Also proposed was a new appendix to Part 50 specifying a reference method for measuring atmospheric lead. The method proposed measures the lead content of suspended particulate matter collected on glass fiber filters using high volume samples. The lead is extracted from the particulate matter and measured by atomic absorption spectroscopy. The procedure proposed is necessarily very restrictive and specific in order to maintain the high level of accuracy and reproducibility and the low level of variability requisit for a reference method. However, other procedures are available for measuring lead which are likely to be as good as the reference method and may be advantageous to particular users. For example, using the same sampling procedure as the reference method (high volume sampler), several alternate analytical principles (flameless atomic absorption, optical emission spectrometry, and anodic stripping voltametry) are known to be suitable for lead analysis.

If these alternate procedures can be designated as "equivalent" methods, then users would have much more flexibility in selecting a method for lead measurements which fits their own circumstances of available equipment, personnel, and expertise.

Also, EPA sees no reason why lead measurements must be restricted to a particular sampling technique, such as the high volume sampler. For example, low volume particulate samples can be analyzed for lead by X-ray fluorescence. Other non-high volume techniques may also be available or under development. By allowing for the possibility of qualifying such alternate methods as equivalent methods, EPA hopes to permit and encourage continued advancement in the technology of measuring atmospheric lead.

For the reasons given above, EPA believes it is advantageous to propose appropriate amendments to 40 CFR Part 53 to extend the equivalent method regulations to cover methods for measuring lead in the atmosphere. Since most, if not all, candidate equivalent methods for lead are likely to be manual methods, EPA expects relatively little initial incentive for commercial organizations to apply for equivalent method determinations. Consequently, most equivalent method applications for lead methods will have to be originated by EPA under section 53.7 "Testing of methods at the Initiative of the Administrator." Specifically, EPA intends to pursue designation of some of the methods noted earlier, which are already in use among some monitoring agencies. These would include methods which use the same sampling procedure as the reference method, but use alternate analytical principles such as flameless atomic absorption, optical emission spectrometry, and

anodic stripping voltametry. Direct analysis of high volume filters by X-ray fluorescence is also a likely candidate method for early designation by EPA.

General Approach

As suggested above, any method which purports to measure atmospheric lead could be considered as a candidate equivalent method, regardless of the sampling procedure or analytical technique used. To be designated as an equivalent method, the candidate method must demonstrate a "consistent relationship" to the reference method. This is done by taking simultaneous measurements with both methods in accordance with the procedures and requirements to be specified in 40 CFR Part 53. In addition, the candidate method must also demonstrate adequate precision among repeated analyses of the same sample.

Since the proposed reference method provides 24-hour integrated measurements, candidate methods would have to be compared on that basis. Shorter-term integrated methods or even automated methods could be considered as candidate methods. But only 24-hour averages could be compared to the reference method. Therefore, any subsequent designation of such a method as an equivalent method would apply only to 24-hour averages.

Amendments to 40 CFR Part 51

Paragraph (a) of section 51.17a provides general requirements

for air quality monitoring methods used by States in their Implementation Plan monitoring networks. Subparagraph (1) requires use of reference or equivalent methods for SO_2, CO, O_3 and NO_2, and would be amended to also include lead. Subparagraph (3) provides certain "grandfather" periods for use of existing methods for SO_2, CO, O_3 and NO_2. It would be amended by adding a similar "grandfather" provision allowing existing methods for lead to be used until February 18, 1980--the same expiration date as that for existing methods for SO_2, CO, and O_3.

Amendments to Part 53

Subpart C of Part 53 contains the test procedures prescribed for determining a consistent relationship between the reference method and a candidate equivalent method. Since these test procedures were originally designed for gaseous pollutants, several significant changes and additions are required to adapt the procedures for lead.

Determination of Consistent Relationship

Section 53.30, paragraph (a) pertaining to the determination of a consistent relationship would be changed to indicate that the specifications for lead appear in a separate table (table C-3) than the specifications for SO_2, CO, O_3 and NO_2.

Test Site

Section 53.30, paragraph (b), pertaining to test sites would be changed in several ways. First, the paragraph would be subdivided to differentiate the various requirements applicable to (1) all methods, (2) methods for gaseous pollutants, and (3) methods for lead. Multiple test sites would be allowed for lead methods in order to facilitate measurements in the required range, since pollutant augmentation would not be feasible for particulate methods. Also, a new provision would allow an applicant to request approval of the test site or sites from EPA prior to conducting the tests.

A final minor change proposed for paragraph (b) would delete the stipulation that test sites be "...away from large bodies of water...". This change has nothing to do with lead, but is prompted by general confusion among applicants as to its specific meaning. Since the requirement is not essential, the current revision of the paragraph provides a good opportunity to eliminate both the stipulation and the confusion.

Other General Provisions

Paragraphs (c), (d), and (e) of section 53.30 would also be revised and reorganized to reflect the differences in requirements for methods for gaseous pollutants and for lead particulates. Revised paragraph (c) specifies the general requirement for simultaneous measurements at the test site in each of the required

concentration ranges indicated by Tables C-1 or C-3. Paragraph
(d) would be revised and subdivided to clarify the different
requirements for sample collection. Subparagraph (1) indicates
the general requirement for homogenous samples. Subparagraph (2)
specifies the use of a common distribution manifold and allows
artificial pollutant augmentation for gaseous pollutants. Sub-
paragraph (3) specifies the relative location requirements for
lead samplers. And paragraph (4) would specifically allow the use
of a common sample when the candidate method uses a sampling
procedure identical to that of the reference method. Finally, the
present paragraph (d) on "Submission of Test Data..." would be
changed to paragraph (e).

Test Conditions

In section 53.31 on "Test Conditions," paragraphs (a), (c),
and (d) would be revised slightly to clarify certain differences
between gaseous and particulate methods, and to clarify the re-
quirements pertaining to calibration and range.

Test Procedures

Because the test procedures being proposed for lead differ
considerably from those for gaseous pollutants, existing section
53.32 would be retitled "Test procedures for gaseous pollutants"
and a new section 53.33, "Test procedures for lead," would be
added. The proposed new section 53.33 is similar in form to

section 53.32, but the specific requirements for lead methods differ in several ways from the requirements for gaseous pollutant methods. First, a new Table C-3 summarizes the test specifications pertinent to methods for lead. Only one concentration range is specified, into which 5 or more of the measurements must fall. The difference specification for lead is specified as a per cent of the reference method measurement, as opposed to the fixed, absolute values specified for gaseous pollutant methods. An accuracy specification for the reference method based on analysis of audit samples supplied by EPA is specified. In addition, a performance specification for analytical precision is also being proposed to apply to lead methods.

Because most methods for lead provide a result only after collected samples are analyzed in a laboratory, the test acceptance criteria are based on a single sampling plan rather than the double sampling plan prescribed for gaseous pollutant methods. Ten or more (simultaneous) samples are collected and analyzed to provide at least 5 samples which fall into the required range of 0.5 to 4.0 $\mu g/m^3$. Each sample is analyzed 3 times and the results of all samples in the range are subjected to both the precision test prescribed in paragraph (e) and the consistent relationship test prescribed in paragraph (f). For the candidate method to qualify for designation, no test failures would be permitted in either test.

Public Participation

Interested persons are invited to comment on any aspect of

these proposed amendments. Comments should be submitted in dup-licate and must be received by [45 days after publication in the Federal Register]. Address comments to:

Mr. Larry Purdue
Department E (MD-76)
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Date

Administrator

It is proposed to amend Chapter I, Title 40, Code of Federal Regulations, as follows:

PART 51--REQUIREMENTS FOR PREPARATION, ADOPTION, AND SUBMITTAL

OF IMPLEMENTATION PLANS

1.   In section 51.17a, paragraph (a) is revised to read as follows:
§51.17a Air quality monitoring methods.

(a) General requirements. (1) Except as otherwise provided in this paragraph (a), each method for measuring SO_2, CO, O_3, NO_2, or lead used for purposes of §51.17(a) shall be a reference method or equivalent method as defined in §53.1 of this chapter. ***

(2) ***

(3) *** Any manual method for lead in use before [date of promulgation of these amendments] may be used for purposes of §51.17(a) until February 18, 1980.

PART 53--AMBIENT AIR MONITORING REFERENCE AND EQUIVALENT
                METHODS

2. In section 53.30, paragraphs (a), (b), (c), (d), and (e) are revised to read as follows:

§53.30 General Provisions

(a) *** A consistent relationship is shown for SO_2, CO, O_3 and NO_2 methods when the differences between (1) measurements made by a candidate manual method or by a test analyzer representative of a candidate automated method, and (2) measurements made simultaneously by a reference method are less than or equal to the value specified in the last column of Table C-1. A consistent relationship is shown for lead methods when the differences between (1) measurements made by a candidate method and (2) measurements made simultaneously by the reference method are less than or equal to the value specified in Table C-3.

(b) Selection of Test Sites. (1) All methods. Each test site shall be in a predominantly urban area which can be shown to have at least moderate concentrations of various pollutants. The site shall be clearly identified and shall be justified as an

appropriate test site with suitable supporting evidence such as maps, population density data, vehicular traffic data, emission inventories, pollutant measurements from previous years, concurrent pollutant measurements and wind or weather data. If desired, a request for approval of the test site or sites may be submitted prior to conducting the tests. The Administrator may in his discretion select a different site (or sites) for any additional tests he decides to conduct.

(2) <u>Methods for gaseous pollutants</u>. All test measurements are to be made at the same test site. If necessary, the concentration of pollutant in the sampled ambient air may be augmented with artificially generated pollutant to facilitate measurements in the specified ranges. (See paragraph (d) (2) of this section.)

(3) <u>Methods for lead</u>. Test measurements may be made at any number of test sites. Augmentation of pollutant concentrations is not permitted, hence an appropriate test site or sites must be selected to provide lead concentrations in the specified range. Test sites for lead measurements must be between 5 and 100 meters from the edge of a heavily-traveled roadway.

(c) <u>Test Atmosphere</u>. Ambient air sampled at an appropriate test site shall be used for these tests. Simultaneous concentration measurements shall be made in each of the concentration ranges specified in Table C-1 or Table C-3.

(d) Sample Collection. (1)   All methods. All test concentration measurements or samples shall be taken in such a way that both the candidate method and the reference method receive air samples that are homogenous or as nearly identical as practical.

(2)   Methods for gaseous pollutants. Ambient air shall be sampled from a common intake and distribution manifold designed to deliver homogenous air samples to both methods. Precautions shall be taken in the design and construction of this manifold to minimize the removal of particulates and trace gases, and to insure that identical samples reach the two methods. If necessary, the concentration of pollutant in the sampled ambient air may be augmented with artificially generated pollutant. However, at all times the air sample measured by the candidate and reference methods under test shall consist of not less than 80 percent ambient air by volume. Schematic drawings, physical illustrations, descriptions, and complete details of the manifold system and the augmentation system (if used) shall be submitted.

(3)   Methods for lead. The intake points of the candidate and reference samplers for lead shall be located between 3 and 5 meters apart, and between 1.5 and 5 meters above ground level.

(4)   Methods employing a common sampling procedure. Candidate methods which employ a sampler and sample collection procedure which are identical to the sampler and sample collection procedure specified in the reference method may be tested by analyzing common samples in accordance with the candidate and refer-

ence analysis procedures. The common samples are to be collected according to the sample collection procedure specified by the reference method, and must be divided such that identical portions are analyzed by the analysis procedures of the two methods.

(e) <u>Submission of Test Data and Other Information</u>. All recorder charts, calibration data, records, test results, procedural descriptions and details, and other documentation obtained from (or pertinent to) these tests shall be identified, date, signed by the analyst performing the test, and submitted.

3. In section 53.31, paragrphs (a), (c), and (d) are revised to read as follows:

§53.31 <u>Test Conditions</u>.

(a) <u>All Methods</u>. All test measurements made or test samples collected by means of a sample manifold as specified in §53.30 (d) (2) shall be at a room temperature between 20° and 30°C, and at a line voltage between 105 and 125 volts. All methods shall be calibrated as specified in paragraph (c) of this section prior to initiation of the tests.

(b) ***

(c) <u>Calibration</u>. The reference method shall be calibrated

according to the appropriate appendix to Part 50 of this Chapter
(if it is a manual method) or according to the applicable operation
manual(s) (if it is an automated method). A candidate manual
method (or portion thereof) shall be calibrated if such calibration
is a part of the method. ***

(d) Range. (1) Except as provided in paragraph (d) (2) of
this section, each method shall be operated in the range specified
for the reference method in the appropriate appendix to Part 50
(for manual reference methods), or specified in Table B-1 of this
part (for automated reference methods).

(2) ***

(e) ***

4. In section 53.32, the title of the section is revised to read
as follows:

§53.32 Test procedures for gaseous pollutants.

* * * * * *

5. A new section is added to read as follows:

§53.33 Test procedure for lead methods.

(a) Sample collection. Collect simultaneous 24-hour samples

(filters) of lead at the test site or sites with both the reference and candidate methods until at least 10 filter pairs have been obtained. If the conditions of §53.30 (d)(4) apply, collect at least 10 common samples (filters) in accordance with §53.30 (d)(4) and divide each to form the filter pairs.

(b) <u>Audit samples</u>. Three audit samples must be obtained from the Director, Environmental Monitoring and Support Laboratory, Department E, United States Environmental Protection Agency, Research Triangle Park, N.C. 27711. The audit samples are 3/4 x 8 inch glass fiber strips containing known amounts of lead at the following nominal levels: 100 µg/strip; 300 µg/strip; 750 µg/strip. The true amount of lead in total µg/strip will be provided with each audit sample.

(c) <u>Filter Analysis</u> . (1) For both the reference method and the audit samples, analysis each filter extract 3 times in accordance with the reference method analytical procedure. The analysis of replicates should not be performed sequentially (i.e. any single sample should not be analyzed 3 times in sequence). Calculate the indicated lead concentrations for the reference method samples in µg/m^3 for each analysis of each filter. Calculate the indicated total lead amount for the audit samples in µg/strip for each analysis of each strip. Label these test results as R_{1A}, R_{1B}, R_{1C}, R_{2A}, R_{2B}, ..., Q_{1A}, Q_{1B}, Q_{1C}, ..., where R denotes results from the reference method samples; Q denotes results from the Audit samples; 1,2,3 indicates filter number and A,B,C indicates the first, second and 3rd analysis of each filter, respectively.

(2) For the candidate method samples, analyze each sample filter or filter extract 3 times and calculate, in accordance with the candidate method, the indicated lead concentration in $\mu g/m^3$ for each analysis of each filter. Label these test results as C_{1A}, C_{1B}, C_{2C}, ..., where C denotes results from the candidate method. (For candidate methods which provide a direct measurement of lead concentrations without a seperable procedure, $C_{1A} = C_{1B} = C_{1C}$, $C_{2A} = C_{2B} = C_{2C}$, etc.)

(d) For the reference method, calculate the average lead concentration for each filter by averaging the concentrations calculated from the 3 analyses:

$$R_{i\ ave} = \frac{R_{iA} + R_{iB} + R_{iC}}{3}$$, where i is the filter number.

(e) Disregard all filter pairs for which the lead concentration as determined in the previous paragraph (d) by the average of the 3 reference method determinations, falls outside the range of 0.5 to 4.0 $\mu g/m^3$. All remaining filter pairs must be subjected to both of the following tests for precision and consistent relationship. At least 5 filter pairs must be within the 0.5 to 4.0 $\mu g/m^3$ range for the tests to be valid.

(f) <u>Test for precision.</u> (1) Calculate the precision (P) of the analysis (in per cent) for each filter and for each method, as the maximum minus the minimum divided by the average of the 3 concentration values, as follows:

$$P_{Ri} = \frac{R_i \max - R_i \min}{R_i \text{ ave}} \times 100\%, \text{ or } P_{Ci} = \frac{C_i \max - C_i \min}{C_i \text{ ave}} \times 100\%,$$

where i indicates the filter number.

(2)   If any reference method precision value (P_{Ri}) exceeds 15 per cent, the precision of the reference method analytical procedure is out of control.   Corrective action must be taken to determine the source(s) of imprecision and the reference method determinations must be repeated according to paragraph (c) of this section, or the entire test procedure (starting with paragraph (a)) must be repeated.

(3)   If any candidate method precision value (P_{Ci}) exceeds 15 per cent, the candidate method fails the precision test.

(4)   The candidate method passes this test if all precision values (i.e. all P_{Ri}'s and all P_{Ci}'s) are less than 15 per cent.

(g)   <u>Test for accuracy.</u>   (1)   For the audit samples calculate the average lead concentration for each strip by averaging the concentrations calculated from the 3 analysis:

$$Q_i \text{ ave} = \frac{Q_{iA} + Q_{iB} + Q_{iC}}{3},$$

where i is audit sample number.

Calculate the percent difference (D_q) between the indicated lead

concentration for each audit sample and the true lead concentration (T_q) as follows:

$$D_{qi} = \frac{Q_i \text{ ave} - T_{qi}}{T_{qi}} \times 100$$

(2) If any difference value (D_{qi}) exceeds ±5 percent the accuracy of the reference method analytical procedure is out of control. Corrective action must be taken to determine the source of the error(s) (e.g. calibration standard discrepancies, extraction problems, etc.) and the reference method and audit sample determinations must be repeated according to paragraph (c) of this section or the entire test procedure (starting with paragraph (a)) must be repeated.

(h) Test for consistent relationship. (1) For each filter pair, calculate all 9 possible percent differences (D) between the reference and candidate methods, using all 9 possible combinations of the 3 determinations (A, B, and C) for each method, as:

$$D_{in} = \frac{C_{ij} - R_{ik}}{R_{ik}} \times 100\%, \text{ where } i \text{ is the filter number, and } n$$

numbers from 1 to 9 for the 9 possible difference combinations for the 3 determinations for each method (j = A, B, C, candidate; k = A, B, C, reference).

(2) If none of the cent differences (D) exceeds ± 20 percent, the candidate method passes the test.

(3) If one or more differences (D) exceeds ± 20 per cent, the candidate method fails the test for consistent relationship.

(i) The candidate method must pass both the precision test and the consistent relationship test to qualify for designation as an equivalent method.

TABLE C-3 TEST SPECIFICATIONS FOR LEAD METHODS.

Concentration range, $\mu g/m^3$:	0.5 to 4.0
Minimum number of 24-hour measurements:	5
Maximum analytical precision, per cent:	15%
Maximum analytical accuracy, per cent:	± 5%
Maximum difference, per cent of reference method:	±20%