INTERNATIONAL STANDARD

ISO 9855

First edition
1993-10-15

Ambient air — Determination of the particulate lead content of aerosols collected on filters — Atomic absorption spectrometric method

Air ambiant — Dosage du plomb dans les particules d'aérosol collectées sur des filtres — Méthode par spectrométrie d'absorption atomique

Reference number
ISO 9855:1993(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 9855 was prepared by Technical Committee ISO/TC 146, *Air quality*, Sub-Committee SC 3, *Ambient atmospheres*.

Annexes A, B and C form an integral part of this International Standard.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Ambient air — Determination of the particulate lead content of aerosols collected on filters — Atomic absorption spectrometric method

1 Scope

This International Standard specifies a method based on acid digestion and atomic absorption spectrometry for the chemical analysis of lead samples collected on filters from ambient air. The method is applicable to ambient air samples with particulate lead contents, such that the amount of deposited particulate lead collected on the filter of the sampling equipment is greater than 1 µg if the final determination is made by flame atomic absorption spectrometry. Final determination by graphite furnace atomic absorption spectrometry allows measurement of quantities of less than 1 µg, but is only applicable after experimental validation of detection limits.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

ISO 6879:1983, *Air quality — Performance characteristics and related concepts for air quality measuring methods.*

ISO 6955:1982, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary.*

3 Principle

Particulate material collected on a filter is digested with acid. Any lead present is solubilized and the sample solution analysed by atomic absorption spectrometry.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity (as in 4.1). It is essential that the lead contents of reagents are constant so that reproducible blank values can be obtained.

4.1 Distilled or deionized water, with a lead content less than 0,01 µg/ml and an electrical conductivity less than 0,2 mS/m (2 µS/cm), or an electrical resistivity greater than 5 kΩ·m.

4.2 Nitric acid (HNO_3), concentrated, ϱ_{20} = 1,42 g/ml, redistilled with a lead content less than 0,01 µg/ml.

4.3 Nitric acid, dilute, approximately 0,1 mol/l.

Add 10 ml of concentrated nitric acid (4.2) to 500 ml of water (4.1) and dilute to 1 litre with water (4.1).

4.4 Lead standard solution, corresponding to 1 000 µg of Pb per millilitre.

Use commercial standard solutions at a concentration of 1 000 µg/ml, or prepare a lead standard solution as follows.

Dissolve 1,598 g ± 0,001 g of lead nitrate [$Pb(NO_3)_2$] previously dried to constant mass at 110 °C and

cooled in a desiccator, in dilute nitric acid (4.3). Quantitatively transfer the solution to a 1 000 ml one-mark volumetric flask (5.1.2) and make up to the mark with dilute nitric acid (4.3).

5 Apparatus

Ordinary laboratory apparatus and

5.1 Glassware, borosilicate.

NOTE 1 It is preferable to reserve a set of glassware for the determination of lead by this method, to ensure that problems do not arise from incomplete removal of contamination.

5.1.1 One-mark pipettes, complying with ISO 648.

5.1.2 One-mark volumetric flasks, of capacities from 10 ml to 1 000 ml, complying with ISO 1042.

5.2 Atomic absorption spectrometer, set up and operated according to the manufacturer's instructions and equipped with: a burner for use with an air/acetylene flame and/or a graphite furnace with auto-injection, a lead hollow cathode lamp or an electrodeless discharge lamp, and a capability for correction of non-specific attenuation (see ISO 6955) by using a deuterium lamp or Zeeman or Smith-Hieftje background correction systems.

5.3 Sampling equipment.

Filters for analysis shall be of a membrane or glass-fibre type. Unexposed filters shall have a maximum lead content considerably lower than the minimum quantity measurable by the atomic absorption procedure used.

6 Sampling

The sampling time shall be sufficient for the amount of lead collected to be large enough for quantitative analysis.

7 Procedure

7.1 Cleaning of glassware

7.1.1 Before use, soak all glassware for 24 h in a mild detergent solution to remove any residual grease or chemicals.

7.1.2 After the initial cleaning (7.1.1), clean all glassware other than pipettes (5.1.1) and volumetric flasks (5.1.2) with hot concentrated nitric acid (4.2) and thoroughly rinse with water (4.1).

7.1.3 After the initial cleaning (7.1.1), clean the pipettes (5.1.1) and volumetric flasks (5.1.2) by soaking in dilute nitric acid (4.3) for several days, and then finally rinse with water (4.1).

Clean glassware which has been through the whole cleaning procedure, and which has been reserved for analysis of lead by this method, by rinsing thoroughly with dilute nitric acid (4.3) and then with water (4.1).

7.2 Calibration

7.2.1 Preparation of calibration solutions

Prepare a calibration blank solution and at least five calibration solutions to cover the range of expected concentrations of the test solutions, within the linear operating range of the atomic absorption spectrometer (5.2), by dilution of the lead standard solution (4.4).

These calibration solutions shall be prepared so that they contain acid concentrations equivalent to those in the final sample solutions obtained using the chosen digestion method (see 7.3.2).

7.2.2 Spectrometric measurements

Set up the atomic absorption spectrometer (5.2) according to the manufacturer's instructions, and optimize the setting of parameters including lamp current and monochromator slit width. For flame atomic absorption spectrometry, optimize burner height, fuel and oxidant flow rates and nebulizer flow rate. For graphite furnace atomic absorption spectrometry, establish the optimum temperature programme to avoid losses of lead, especially during the ashing phase of the temperature programme. Do not use graphite furnace atomic absorption spectrometry without auto-injection. In all cases, correction for non-specific attenuation shall be used.

7.2.3 Plotting the calibration curve

Prepare a calibration graph by plotting the absorbance of each calibration solution with respect to the absorbance of the calibration blank solution, versus the concentration of lead in the calibration solutions, in micrograms per millilitre (or, if graphite furnace atomic absorption spectrometry is used, in micrograms per litre).

7.3 Determination

7.3.1 Blank filter

Analyse at least one unexposed filter with each batch of exposed test filters.

7.3.2 Acid digestion of filters

Carry out the digestion of sample and blank filters using one of the methods specified in annexes A to C. The method specified in annex A (digestion with nitric acid and hydrochloric acid) is the reference method. Use the method specified in annex B (digestion with nitric acid and hydrogen peroxide) or the method specified in annex C (digestion with nitric acid under pressure) only after demonstrating that these methods achieve complete analytical recovery.

NOTE 2 This demonstration should be based on measuring the recoveries obtained by using the method specified in annex B or C on equivalent samples to those being analysed, and then comparing the results with those obtained using the reference method specified in annex A. The reference method should always be used where incomplete recovery is indicated by measurements or visual evidence of undissolved residues.

7.3.3 Spectrometric measurement

Determine the concentration of lead in the sample solutions (7.3.2) using either flame or graphite furnace atomic absorption spectrometry, by measuring the absorbance at a wavelength of 217,0 nm or 283,3 nm, with correction for non-specific attenuation.

The sample concentration is related to the absorbance, and can be determined from the appropriate calibration graph (7.2.3). Use only the linear part of the calibration curve and dilute the test solutions whose response falls outside this region with an appropriate volume of dilute nitric acid (4.3). Record the dilution factor used. For the graphite furnace procedure, use the same final sampling volume for both analysis and calibration.

7.3.4 Blank solutions

Analyse all of the blank solutions (7.3.1), and subtract the mean lead concentration of the blank solutions from the lead concentration of the sample solutions. Where sample solutions are diluted into the linear operating range of the atomic absorption spectrometer, an equivalent dilution shall be made of the blank solutions; and the mean lead concentration of this diluted blank solution subtracted from the lead content of the diluted sample solutions. Use standardized statistical methods (see ISO 6879) to determine the detection limit, based on the standard deviation of the lead concentration in a minimum of six solutions obtained by dissolution of blank filters.

8 Expression of results

Express the mass concentration of lead ϱ_{Pb}, in micrograms per cubic metre, in the air sample to the nearest 0,1 µg/m^3, using the equation

$$\varrho_{Pb} = \frac{(\varrho_{Pb,1} - \varrho_{Pb,2})V_1 \cdot F}{V_{corr}}$$

where

$\varrho_{Pb,1}$ is the concentration of lead, in micrograms per millilitre, in the sample solution;

$\varrho_{Pb,2}$ is the mean concentration of lead, in micrograms per millilitre, in the solutions obtained by digestion of unexposed filters;

V_1 is the volume, in millilitres, to which the sample ash was diluted (e.g. 10 ml);

F is the dilution factor used (if applicable);

V_{corr} is the corrected volume, in cubic metres, of the air sample.

9 Performance of methods

The application of this International Standard to blank membrane and glass-fibre filters has demonstrated that a detection limit of 1 µg is achievable using either of the three specified digestion methods. When the digestion method specified in annex A (the reference method) was applied to filters spiked with an urban particulate reference material, the recovery of lead relative to the certified value was 99,2 % ± 4,3 % for the spiked membrane filters and 101,0 % ± 6,0 % for the spiked glass-fibre filters.

10 Interferences

The method may not be suitable for samples with high ratios between an interfering element and lead. The nature and extent of interferences depends on whether flame or graphite furnace atomic absorption spectrometry is used. The only major spectral interference which is likely to occur is due to antimony when a wavelength of 217,0 nm is used. Where high concentrations of sodium are present in sample solutions, efficient correction of non-specific background absorbance is essential.

11 Test report

The test report shall include at least the following information:

a) all details necessary for the complete identification of the air sample, including details of the type of sampling equipment used;

b) a reference to this International Standard;

c) which sample digestion method was used;

d) the concentration of lead found, in micrograms per cubic metre, and the analytical variables used: i.e. final extract volume, dilution/concentration step factors, readings in micrograms per millilitre, and blank values;

e) the type of atomic absorption spectrometer used;

f) any operational details not specified in this International Standard, as well as any circumstances likely to have influenced the test result.

Annex A
(normative)

Filter digestion by reflux with nitric acid and hydrochloric acid

A.1 Principle

Particulate material collected on a filter is digested by refluxing with nitric acid and hydrochloric acid.

A.2 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity. See clause 4 .

A.2.1 Nitric acid, concentrated.

See 4.2.

A.2.2 Hydrochloric acid (HCl), concentrated, $\varrho_{20} = 1{,}18$ g/ml, with a lead content less than 0,01 µg/ml.

A.2.3 Digestion acid.

Mix 1 volume of concentrated nitric acid (A.2.1) with 2 volumes of concentrated hydrochloric acid (A.2.2).

A.3 Apparatus

A.3.1 Glassware, borosilicate.

(See 7.1 for cleaning instructions.)

A.3.1.1 Conical flasks, of capacity 100 ml with ground-glass necks.

A.3.1.2 Reflux condensers, with ground-glass joints to fit the necks of conical flasks (A.3.1.1).

A.3.1.3 Measuring cylinder, of capacity 100 ml.

A.3.1.4 One-mark volumetric flasks, of capacity 50 ml, complying with ISO 1042.

A.3.2 Hotplate, thermostatically controlled.

A.4 Digestion procedure for membrane filters

Place the filter in a conical flask (A.3.1.1), add 10 ml of digestion acid (A.2.3) and connect to a reflux condenser (A.3.1.2). Place the conical flask on a hotplate (A.3.2), raise the temperature of the hotplate to 100 °C ± 5 °C and continue heating the flask for 2 h. Allow the apparatus to cool. Wash the inside of the condenser down into the conical flask, with repeated small volumes of water. Then transfer the digest to a 50 ml volumetric flask (A.3.1.4) and dilute to volume with distilled water.

A.5 Digestion procedure for glass-fibre filters

Follow the digestion procedure for membrane filters (A.4), until the digest is ready to be transferred to the volumetric flask. Then filter, with repeated small washings of water, into a 50 ml volumetric flask (A.3.1.4).

Annex B
(normative)

Filter digestion with nitric acid and hydrogen peroxide

B.1 Principle

Particulate material collected on a filter is digested with nitric acid and hydrogen peroxide.

B.2 Reagents

Use only reagents on recognized analytical grade and only distilled water or water of equivalent purity. See clause 4.

B.2.1 Nitric acid, concentrated.

See 4.2.

B.2.2 Nitric acid, dilute.

See 4.3.

B.2.3 Hydrogen peroxide (H_2O_2), approximately 300 g/l (100 volumes), with a lead content less than 0,01 µg/ml.

B.3 Apparatus

B.3.1 Glassware, borosilicate.

(See 7.1 for cleaning instructions.)

B.3.1.1 Beakers, of capacity 50 ml.

B.3.1.2 Watch glasses, to fit the beakers (B.3.1.1).

B.3.1.3 Measuring cylinder, of capacity 100 ml.

B.3.1.4 One-mark pipettes, complying with ISO 648.

B.3.1.5 One-mark volumetric flasks, of capacities 10 ml and 25 ml, complying with ISO 1042.

B.3.2 Hotplate, thermostatically controlled.

B.4 Digestion procedure for membrane filters

Add 3 ml of concentrated nitric acid (B.2.1) and 1 ml of hydrogen peroxide (B.2.3) to the filter in a 50 ml beaker (B.3.1.1). Cover with a watch glass (B.3.1.2) and heat on a hotplate (B.3.2) to 180 °C ± 5 °C until most of the acid has evaporated. Repeat this addition of acid and hydrogen peroxide, followed by evaporation, at least twice. Then, continue to heat until the residue is barely dry and a white ash appears. Do not bake the residue. If the residue ignites, discard the sample, as lead will have been lost. Rinse the watch glass and the sides of the beaker with a small volume of dilute nitric acid (B.2.2). Replace the watch glass and evaporate until the residue is almost dry. Cool and add 1 ml of concentrated nitric acid (B.2.1) to dissolve the residue. Transfer, with further washings of dilute nitric acid (B.2.2), to a 10 ml volumetric flask (B.3.1.5) and make up to the mark with dilute nitric acid.

B.5 Digestion procedure for glass-fibre filters

Follow the procedure for membrane filters (B.4) until the final evaporation of acid. Dissolve the residue in 2,5 ml of concentrated nitric acid (B.2.1). Filter the digest, with repeated small washings of dilute nitric acid (B.2.2), into a 25 ml volumetric flask (B.3.1.5), and then make up to the mark with dilute nitric acid.

Annex C
(normative)

Filter digestion under pressure with nitric acid

C.1 Principle

Particulate material collected on a filter is digested with nitric acid, using a polytetrafluoroethylene (PTFE)-lined pressure digestion vessel.

C.2 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity. See clause 4.

C.2.1 Nitric acid, concentrated.

See 4.2.

C.2.2 Nitric acid, dilute.

See 4.3.

C.3 Apparatus

C.3.1 Glassware, borosilicate.

(See 7.1 for cleaning instructions.)

C.3.1.1 One-mark pipettes, complying with ISO 648.

C.3.1.2 One-mark volumetric flasks, of capacities 10 ml and 25 ml, complying with ISO 1042.

C.3.2 Pressure digestion vessel, consisting of a stainless steel outer vessel and lid, containing a PTFE inner vessel and lid. The volume of the inner vessel shall be at least 20 ml. The vessel shall be capable of resisting a temperature of at least 190 °C and pressures higher than 20 MPa. The vessel shall be provided with a safety valve to vent excessive pressure.

C.3.3 Oven or heating block, thermostatically controlled, capable of operating at 180 °C ± 2 °C and fitted with a safety switch actuated at a temperature of 190 °C.

C.4 Digestion procedure for membrane filters

Add 1 ml of concentrated nitric acid (C.2.1) to the filter in the PTFE inner vessel of the pressure digestion vessel (C.3.2). Close the inner vessel with its PTFE lid and place it in the stainless steel outer vessel. Close the outer vessel with the steel lid up to the prescribed torque. Place the complete assembly in the oven or heating block (C.3.3). Heat at 180 °C for 12 h, and then allow the vessel and oven or heating block to cool completely to ambient temperature.

Open the cold digestion vessel and remove the PTFE inner vessel. Using a pipette (C.3.1.1) quantitatively transfer the digest, together with repeated small washings of dilute nitric acid (C.2.2), to a 10 ml volumetric flask (C.3.1.2), and make up to the mark with dilute nitric acid.