International Standard 6503

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Paints and varnishes — Determination of total lead — Flame atomic absorption spectrometric method

Peintures et vernis — Détermination du plomb total — Méthode par spectrométrie d'absorption atomique dans la flamme

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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Contents

INTERNATIONAL STANDARD ISO 6503-1984 (E)

Paints and varnishes — Determination of total lead — Flame atomic absorption spectrometric method

1 Scope and field of application

This International Standard describes a flame atomic absorption spectrometric method for the determination of total lead in paints and related products.

The method is applicable to products having total lead contents in the range of about 0,01 to 2 % (*m/m*).

NOTE — This method may also be applicable to products with a total lead content of more than 2 % (*m/m*), but it should only be used when the precision does not exceed the appropriate values given in 7.2.

Two methods are given for the treatment of the test portion; the dry ashing method (clause 4) should be used as the referee method in cases of dispute.

For the determination of lead in the test solution, the dithizone spectrophotometric method specified in ISO 3856/1 may be used as an alternative method.

2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1 : General requirements.* [1]

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

ISO 1512, *Paints and varnishes — Sampling.*

ISO 1513, *Paints and varnishes — Examination and preparation of samples for testing.*

ISO 3696, *Water for laboratory use — Specifications.* [2]

ISO 3856/1, *Paints and varnishes — Determination of "soluble" metal content — Part 1 : Determination of lead content — Flame atomic absorption spectrometric method and dithizone spectrophotometric method.*

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

3 Principle

Decomposition of a test portion by either the dry ashing method (clause 4) or the wet oxidation method (clause 5), and determination of the lead by flame atomic absorption spectrometry.

4 Dry ashing method

4.1 Principle

Evaporation of a test portion to dryness and ashing at 475 °C to remove all organic matter. Extraction of any lead in the residue with hydrochloric acid.

4.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity according to ISO 3696.

4.2.1 Sodium carbonate, anhydrous.

4.2.2 Magnesium carbonate.

4.2.3 Sulfur.

4.2.4 Liquid paraffin.

4.2.5 Sodium sulfide, 10 g/l solution.

4.2.6 Hydrochloric acid, approximately 180 g/l.

Add 450 ml of concentrated hydrochloric acid [36 % (*m/m*), ϱ approximately 1,18 g/ml] to an approximately equal amount of water and dilute to 1 000 ml.

4.2.7 Hydrochloric acid, approximately 18 g/l.

Add 100 ml of the hydrochloric acid (4.2.6) to water and dilute to 1 000 ml.

1) At present at the stage of draft. (Partial revision of ISO/R 385-1964.)

2) At present at the stage of draft.

4.2.8 Nitric acid, approximately 315 g/l.

Add 1 volume of concentrated nitric acid [about 65 % (m/m), ϱ approximately 1,40 g/ml] to 2 volumes of water.

4.2.9 Lead, standard stock solution containing 1 g of Pb per litre.

Either

a) transfer the contents of an ampoule of standard lead solution containing exactly 1 g of Pb into a 1 000 ml one-mark volumetric flask containing some water and 30 ml of the nitric acid (4.2.8), dilute to the mark with water and mix well;

or

b) weigh, to the nearest 1 mg, 1,598 g of lead nitrate [$Pb(NO_3)_2$] (previously dried for 2 h at 105 °C), dissolve in water in a 1 000 ml one-mark volumetric flask, add 30 ml of the nitric acid (4.2.8), dilute to the mark with water and mix well.

1 ml of this standard stock solution contains 1 mg of Pb.

4.2.10 Lead, standard solution containing 100 mg of Pb per litre.

Prepare this solution on the day of use.

Pipette 10 ml of the standard stock solution (4.2.9) into a 100 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid (4.2.7) and mix well.

1 ml of this standard solution contains 100 µg of Pb.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Crucibles, silica, preferably new.

4.3.2 Muffle furnace, capable of being maintained at 475 ± 25 °C.

4.3.3 Hotplate, with energy regulation control.

4.4 Sampling

Take a representative sample of the product to be tested by the method described in ISO 1512.

Examine and prepare the sample for testing as described in ISO 1513.

4.5 Procedure

4.5.1 Preliminary tests

If the composition of the product to be tested is not known, carry out qualitative tests for the presence of cellulose nitrate and antimony. If the results of these tests do not confirm the absence of cellulose nitrate and antimony, carry out the full procedure.

4.5.2 Test portion

Carry out the procedure in duplicate.

Mix the sample thoroughly and immediately transfer about 5 g into a weighed silica crucible (4.3.1). Weigh the test portion to the nearest 10 mg.

If the product contains cellulose nitrate (see 4.5.1), mix about 2 g of the liquid paraffin (4.2.4) with the test portion in the crucible.

4.5.3 Ashing

Place the crucible and its contents on the hotplate (4.3.3) in a fume cupboard. Gradually increase the temperature of the hotplate to remove all volatile solvents.

Spread 2 g of the magnesium carbonate (4.2.2) over the contents of the crucible and, over a period of 10 min, progressively introduce the crucible into the muffle furnace (4.3.2) at approximately 350 °C. Raise the temperature of the furnace to 475 ± 25 °C over a further period of 60 min and maintain at this temperature until ashing is complete. Ensure that an adequate supply of air for oxidation is available.

Do not allow the material in the crucible to ignite at any stage.

4.5.4 Extraction

4.5.4.1 If the material does not contain antimony (see 4.5.1), proceed as follows.

Allow the crucible and ash (see 4.5.3) to cool. Transfer the crucible and ash to a 250 ml beaker, add 100 ml of the hydrochloric acid (4.2.6) and, using the hotplate (4.3.3), boil gently for 15 min. Then allow to digest for a further 15 min.

While still hot, filter by decantation through a fine-texture filter paper[1], into a 250 ml beaker. Wash the paper and residue with hot water, collecting the washings in the beaker. Cool the beaker and transfer the filtrate and washings to a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1) The following filter papers have been found to be suitable :

Whatman Nos. 42 and 44
Schleicher and Schüll Nos. 589/3 and 589/6.

4.5.4.2 If the material contains antimony (see 4.5.1), proceed as follows.

Grind the ash (see 4.5.3) to a fine powder, replace it in the same crucible and mix it with approximately 10 g of a mixture of equal parts of the sodium carbonate (4.2.1) and the sulfur (4.2.3). Cover the crucible and heat it over a moderate flame until there is no odour of sulfur dioxide; this should take 1 to 2 h.

Cool the crucible and digest the contents with a small quantity of hot water until the melt is completely broken up. Filter, transferring all the residue to a filter paper with the sodium sulfide solution (4.2.5) and wash the residue with the sodium sulfide solution. Reject the filtrate.

Transfer the filter paper and residue to a 250 ml beaker. Add 15 ml of the nitric acid (4.2.8) and, using the hotplate (4.3.3), boil gently for 15 min. Add 100 ml of the hydrochloric acid (4.2.6) and allow to digest for 30 min. While still hot, filter through a fine-texture filter paper into a 250 ml beaker. Wash the paper and residue with hot water, collecting the washings in the beaker. Cool the beaker and transfer the filtrate and washings to a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

4.5.5 Preparation of test solutions

From each extract solution (4.5.4) take an aliquot portion, of size determined by the expected lead content in the sample, in accordance with table 1.

Table 1

Expected lead content	Aliquot portion
% (m/m)	ml
less than 0,4	25
0,4 to 1	10
1 to 2	5

NOTE — If the lead content is higher than 2 % (m/m), a suitable aliquot portion should be taken.

Place the aliquot portion in a 100 ml one-mark volumetric flask and, if a 5 ml or 10 ml aliquot portion is taken, add 10 ml of the hydrochloric acid (4.2.6). Dilute to the mark with water and mix well.

4.5.6 Preparation of reagent blank

Repeat the procedures described in 4.5.3, 4.5.4.1 or 4.5.4.2 and 4.5.5, but omitting the test portion.

5 Wet oxidation method

5.1 Principle

Wet oxidation of a test portion with a mixture of sulfuric acid and hydrogen peroxide in a beaker (method A) or with a mixture of sulfuric acid and nitric acid in a Kjeldahl flask (method B) to remove all organic matter. Heating to remove the excess sulfuric acid, and extraction of any lead (in the form of lead sulfate) in the residue with EDTA and ammonia solution.

NOTE — The presence of antimony or cellulose nitrate in a sample does not cause interference with this method.

5.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity according to ISO 3696.

5.2.1 Sulfuric acid, about 96 % (m/m), ϱ approximately 1,84 g/ml.

5.2.2 Hydrogen peroxide, approximately 30 % (m/m), or, with the appropriate additional safety precautions, approximately 50 % (m/m) solution.

5.2.3 Nitric acid, about 65 % (m/m), ϱ approximately 1,40 g/ml.

5.2.4 Nitric acid, approximately 315 g/l.

Add 1 volume of the nitric acid (5.2.3) to 2 volumes of water.

5.2.5 Ammonia solution, approximately 85 g NH_3/l solution.

Dilute 380 ml of concentrated ammonia solution [25 % (m/m)] to 1 000 ml with water.

5.2.6 EDTA (Ethylenediaminetetraacetic acid, disodium salt), 37 g/l solution.

5.2.7 Lead, standard stock solution containing 1 g of Pb per litre.

Either

a) tranfer the contents of an ampoule of standard lead solution containing exactly 1 g of Pb into a 1 000 ml one-mark volumetric flask containing some water and 30 ml of the nitric acid (5.2.4), dilute to the mark with water and mix well;

or

b) weigh to the nearest 1 mg, 1,598 g of lead nitrate [$Pb(NO_3)_2$] (previously dried for 2 h at 105 °C), dissolve in water in a 1 000 ml one-mark volumetric flask, add 30 ml of the nitric acid (5.2.4), dilute to the mark with water and mix well.

1 ml of this standard stock solution contains 1 mg of Pb.

5.2.8 Lead, standard solution containing 100 mg of Pb per litre.

Prepare this solution on the day of use.

Pipette 10 ml of the standard stock solution (5.2.7) into a 100 ml one-mark volumetric flask, add 10 ml of the nitric acid (5.2.4), dilute to the mark with water and mix well.

1 ml of this standard solution contains 100 µg of Pb.

5.3 Apparatus

Ordinary laboratory apparatus and

5.3.1 Hotplate, with energy regulation control.

5.4 Sampling

Take a representative sample of the product to be tested by the method described in ISO 1512.

Examine and prepare the sample for testing as described in ISO 1513.

5.5 Procedure

5.5.1 Test portion

Carry out the procedure in duplicate.

Mix the sample thoroughly and immediately transfer about 0,5 g into a 400 ml beaker (method A) or into a 250 ml Kjeldahl flask (method B). Weigh the test portion to the nearest 1 mg.

5.5.2 Decomposition

5.5.2.1 Method A

Place the beaker and its contents on the hotplate (5.3.1) in a fume cupboard and heat gently to remove all volatile solvents. Add about 5 ml of the sulfuric acid (5.2.1), cover the beaker with a watch glass and heat for about 15 min at a higher temperature to decompose and carbonize the organic substances. Continue heating until white fumes are evolved.

Take the beaker from the hotplate and allow to cool for about 10 min. Add slowly, from a 5 ml pipette, four 5 ml portions of the hydrogen peroxide solution (5.2.2), allowing the reaction to subside after each addition (see WARNING).

WARNING — Because of the danger from spattering, the beaker should be kept covered between additions of hydrogen peroxide solution.

Heat again for about 10 min and allow to cool for 5 min. Then add two further 5 ml portions of the hydrogen peroxide solution, heat for 5 min and allow to cool for 5 min. Finally add one further 5 ml portion of the hydrogen peroxide solution. Heat again to decompose the remaining hydrogen peroxide. Remove the watch glass and carefully rinse the underside with water, collecting the rinsings in the beaker. Heat the beaker until copious white fumes are evolved and the solution has evaporated almost to dryness. Remove the beaker from the hotplate and allow to cool.

5.5.2.2 Method B

Heat gently the Kjeldahl flask and its contents with a Bunsen burner to remove all volatile solvents. Add about 5 ml of the sulfuric acid (5.2.1) and heat for about 10 min to decompose and carbonize the organic substances. Allow to cool for about 10 min. Add slowly, from a 5 ml pipette, four 5 ml portions of the nitric acid (5.2.3), allowing the reaction to subside after each addition.

Heat again for about 10 min and allow to cool for 5 min. Then add two further 5 ml portions of the nitric acid, heat for 5 min and allow to cool for 5 min. Finally add one further 5 ml portion of the nitric acid. Heat again to decompose all the nitric acid and until copious white fumes are evolved and the solution has evaporated almost to dryness. Allow to cool. If charring occurs during this final stage, carefully add further portions of the nitric acid and repeat the heating, fuming and cooling procedure.

5.5.3 Extraction

Add to the beaker (method A) or the Kjeldahl flask (method B), 50 ml of the EDTA solution (5.2.6), 10 ml of the ammonia solution (5.2.5) and 50 ml of water. Boil gently for about 15 min, cool and, if necessary, filter by decantation through a medium texture filter paper into a 250 ml one-mark volumetric flask, washing the paper and the residue with water. Dilute to the mark with water and mix well.

5.5.4 Preparation of test solutions

From each extract solution (5.5.3) take an aliquot portion, of size determined by the expected lead content in the sample, in accordance with table 2.

Table 2

Expected lead content	Aliquot portion
% (*m*/*m*)	ml
less than 0,5	100 (undiluted)
0,5 to 1	75
1 to 2	50

NOTE — If the lead content is more than 2 % (*m*/*m*), a suitable aliquot portion should be taken.

Place the aliquot portion in a 100 ml one-mark volumetric flask, dilute to the mark with water and mix well.

5.5.5 Preparation of reagent blank

Repeat the procedures described in 5.5.2.1 (method A) or 5.5.2.2 (method B), 5.5.3 and 5.5.4, but omitting the test portion.

6 Determination

6.1 Principle

Aspiration of the test solution into an acetylene/air flame. Measurement of the absorption of the selected spectral line

emitted by a lead hollow-cathode lamp or lead discharge lamp in the region of 283,3 nm.

6.2 Reagents and materials

During the analysis, use only reagents of recognized analytical grade and only distilled water or water or equivalent purity.

6.2.1 Acetylene, commercial grade, in a steel cylinder.

6.2.2 Compressed air.

6.3 Apparatus

Ordinary laboratory apparatus and

6.3.1 Flame atomic absorption spectrometer, suitable for measurements at a wavelength of 283,3 nm and fitted with a burner fed with acetylene and air.

6.3.2 Lead hollow-cathode lamp or **lead discharge lamp.**

6.3.3 Burette, of capacity 50 ml, complying with the requirements of ISO 385/1.

6.3.4 One-mark volumetric flasks, of capacity 100 ml, complying with the requirements of ISO 1042.

6.4 Procedure

6.4.1 Preparation of the calibration graph

Either prepare a calibration graph as described below or use a method of instrumental calibration of at least equivalent accuracy and precision.

6.4.1.1 Preparation of the standard matching solutions

Prepare these solutions on the day of use.

Into a series of six 100 ml one-mark volumetric flasks (6.3.4), introduce from the burette (6.3.3), respectively, the volumes of the standard lead solution (4.2.10 or 5.2.8) shown in table 3. Add 10 ml of the hydrochloric acid (4.2.6) to each, dilute to the mark with water and mix well.

Table 3

Standard matching solution No.	Volume of the standard lead solution (4.2.10 or 5.2.8 as appropriate)	Corresponding concentration of Pb in the standard matching solution
	ml	µg/ml
0*	0	0
1	2	2
2	5	5
3	10	10
4	20	20
5	30	30

* Blank matching solution.

6.4.1.2 Spectrometric measurements

Install the lead spectral source (6.3.2) in the spectrometer (6.3.1) and optimize the conditions for the determination of lead. Adjust the instrument in accordance with the manufacturer's instructions and adjust the monochromator to the region of 283,3 nm in order to obtain the maximum absorbance.

Adjust the flow of the acetylene (6.2.1) and of the air (6.2.2) according to the characteristics of the aspirator-burner, and ignite the flame. Set the scale expansion, if fitted, so that the standard matching solution No. 5 (see table 3) gives almost a full scale deflection.

Aspirate into the flame each of the standard matching solutions (see 6.4.1.1) in ascending order of concentration, and repeat with the standard matching solution No. 4 to verify that the instrument has achieved stability. Aspirate water through the burner between each measurement, taking care to keep the rate of aspiration uniform.

6.4.1.3 Calibration graph

Plot a graph having the masses, in micrograms, of Pb contained in 1 ml of the standard matching solutions as abscissae and the corresponding values of the absorbances, reduced by the reading for the blank matching solution as ordinates.

6.4.2 Determination

6.4.2.1 Measure first the absorbance of the blank test solution (4.5.6 or 5.5.5) in the spectrometer (6.3.1) after having adjusted it as described in 6.4.1.2. Then measure the absorbance of each test solution (4.5.5 or 5.5.4) three times and, afterwards, that of the blank test solution again. Finally, redetermine the absorbance of standard matching solution No. 4 (see table 3) in order to verify that the response of the apparatus has not changed. If the absorbance of a test solution is higher than that of the standard matching solution with the highest lead concentration, dilute the test solution appropriately (dilution factor F) with a known volume of water.

6.4.2.2 If the readings obtained for a test solution differ by more than 2 % or by more than 1 % of their mean, repeat the procedures described in 6.4.2.1.

6.4.2.3 From the absorbance, corrected for the reagent blank, determine the concentration, c, of lead in each test solution using the calibration graph. If a direct reading instrument is used, record the lead concentration registered by the instrument.

7 Expression of results

7.1 Calculation

Calculate the lead content of the paint, using the equation

$$a = \frac{2{,}5 \times c \times F}{m \times V}$$

where

a is the total lead content of the paint, expressed as a percentage by mass;

c is the lead concentration, in micrograms per millilitre, of the test solution, obtained from the calibration graph;

F is the dilution factor referred to in 6.4.2.1;

m is the mass, in grams, of the test portion (4.5.2 or 5.5.1);

V is the volume, in millilitres, of the aliquot portion of the extract taken in 4.5.5 or 5.5.4.

Calculate the mean of the two results.

7.2 Precision

NOTE — The following values are based on the calculating procedure described in ISO 5725, using the experimental data available. They are subject to revision as further experience of the procedure is obtained.

7.2.1 Repeatability (r)

The value below which the absolute difference between two single test results on identical material, obtained within a short interval of time by one operator in one laboratory using the same equipment and the standardized test method, may be expected to lie with a 95 % probability is

5 % relative to the mean value for the dry ashing procedure described in 4.5.4.1;

10 % relative to the mean value for the dry ashing procedure with antimony extraction described in 4.5.4.2;

5 % relative to the mean value for the wet oxidation procedure described in 5.5.2.1 (see the note 2 to 7.2.2).

7.2.2 Reproducibility (R)

The value below which the absolute difference between two single test results on identical material, obtained by operators in different laboratories using the standardized test method, may be expected to lie with a 95 % probability is

15 % relative to the mean value for the dry ashing procedure described in 4.5.4.1;

30 % relative to the mean value for the dry ashing procedure with antimony extraction described in 4.5.4.2;

15 % relative to the mean value for the wet oxidation procedure described in 5.5.2.1 (see notes).

NOTES

1 The precision data presented for the wet oxidation procedure described in 5.5.2.1 (Method A) are based on a single paint sample.

2 No data are available for the wet oxidation procedure described in 5.5.2.2 (Method B).

8 Test report

The test report shall contain at least the following information :

a) the type and identification of the product tested;

b) a reference to this International Standard (ISO 6503);

c) the method used for the extraction of lead from the product under test (dry ashing or wet oxidation method) and, if the wet oxidation method was used, record the decomposition procedure used; method A or method B);

d) any preliminary treatment carried out in accordance with 4.5.2;

e) the result of the test;

f) any deviation, by agreement or otherwise, from the procedure specified;

g) the date of the test.