INTERNATIONAL STANDARD

ISO 11441

First edition
1995-02-15

Corrected and reprinted
1995-08-01

Lead sulfide concentrates — Determination of lead content — Back titration of EDTA after precipitation of lead sulfate

Concentrés sulfurés de plomb — Dosage du plomb — Titrage en retour de l'EDTA après précipitation du sulfate de plomb

Reference number
ISO 11441:1995(E)

Contents

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

Printed in Switzerland

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 11441 was prepared by Technical Committee ISO/TC 183, *Copper, lead and zinc ores and concentrates*.

Annexes A and B form an integral part of this International Standard. Annex C is for information only.

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Lead sulfide concentrates — Determination of lead content — Back titration of EDTA after precipitation of lead sulfate

1 Scope

This International Standard specifies a lead sulfate precipitation EDTA titrimetric method for the determination of lead content in lead sulfide concentrates.

The method is applicable to all lead sulfide concentrates with lead content in the range from 10 % (*m/m*) to 80 % (*m/m*).

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 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

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

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

ISO 4787:1984, *Laboratory glassware — Volumetric glassware — Methods for use and testing of capacity.*

ISO 9599:1991, *Copper, lead and zinc sulfide concentrates — Determination of hygroscopic moisture in the analysis sample — Gravimetric method.*

ISO Guide 35:1989, *Certification of reference materials — General and statistical principles.*

3 Principle

The stages which comprise the determination are described in 3.1 to 3.4 inclusive.

3.1 Dissolution

Dissolution by fusion with sodium peroxide.

3.2 Precipitation

Double precipitation of lead as a sulfate, with removal of bismuth if applicable.

3.3 EDTA dissolution

Dissolution of lead sulfate in a known volume of an alkaline EDTA solution.

3.4 Titration

Titration of EDTA in excess by a titrated zinc solution.

4 Reagents

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

4.1 Lead metal, minimum 99,99 % purity.

The surface of the metal shall be free from oxide prior to use and may be cleaned by immersing the metal in nitric acid solution (4.10) diluted 1 + 9 for 1 min, washed well with water followed by acetone and dried in an oven at 50 °C.

4.2 Zinc metal, minimum 99,99 % purity.

The surface of the metal shall be free from oxide prior to use and may be cleaned by immersing the metal in nitric acid (4.10) diluted 1 + 9 for 1 min, washed well with water followed by acetone and dried in an oven at 50 °C.

4.3 Sodium peroxide.

4.4 Sodium fluoride.

4.5 Perchloric acid, (ρ_{20} 1,70 g/ml).

4.6 Hydrogen peroxide, at 100 volumes.

4.7 Ethanol, at 95 % (*V/V*).

4.8 Hydrofluoric acid, concentrated (ρ_{20} 1,15 g/ml)

WARNING — Even when diluted hydrofluoric acid is extremely dangerous and harmful to the eyes and skin; rubber gloves and goggles should be worn when using this acid. Hydrofluoric acid attacks glassware. Care should be taken to minimize the time of acid contact with glassware. Use only in a mechanically ventilated fume cupboard.

4.9 Sulfuric acid, concentrated (ρ_{20} 1,83 g/ml).

4.10 Nitric acid, concentrated (ρ_{20} 1,42 g/ml).

4.11 Hydrochloric acid, concentrated (ρ_{20} 1,16 g/ml to 1,19 g/ml).

4.12 Acid washing mixture

Mix 50 ml of perchloric acid (4.5) with 100 ml of hot water and add 2 ml of hydrogen peroxide (4.6). (To be freshly prepared just before use.)

4.13 Sulfuric acid, diluted 1 + 1

Slowly add 500 ml of concentrated sulfuric acid (4.9) to 500 ml of water. Mix thoroughly.

4.14 Washing solution

Mix 200 ml of water with 100 ml of ethanol (4.7) and 50 ml of sulfuric acid (4.13). Mix thoroughly.

4.15 Potassium hydroxide solution

Dissolve 200 g of potassium hydroxide in water. Dilute to 1 litre and mix. Store in plastic bottles.

4.16 Nitric acid, diluted 1 + 1

Slowly add 500 ml of concentrated nitric acid (4.10) to 500 ml of water. Mix thoroughly.

4.17 Zirconium nitrate solution

Add 3,53 g of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) to 20 ml of nitric acid (4.10). Boil for approximately 10 min. Cool to room temperature. Dilute to 1 litre with water and mix.

4.18 Basic washing solution

Dilute 50 ml of the potassium hydroxide solution (4.15) to 1 litre with water.

4.19 Ammonium acetate solution

Dissolve 500 g of ammonium acetate in water. Dilute to 1 litre and mix.

4.20 Aqueous hexamethylene tetramine solution, saturated at room temperature.

4.21 Solution of disodium salt of ethylenediaminetetraacetic acid, $c(\text{EDTA}) = 0{,}1$ mol/l. Dissolve 37,22 g of disodium versenate in water, dilute to 1 litre and mix.

NOTE 1 The procedure for standardizing the EDTA solution is given in 4.22.2.

4.22 Standard solutions

NOTE 2 Standard solutions should be prepared at the same ambient temperature as that at which the determinations will be conducted.

4.22.1 Zinc standard solution, $c\left(Zn^{2+}\right) = 0{,}1$ mol/l

4.22.1.1 Preparation

Place 6,537 g of pure, freshly prepared, unoxidized zinc chips (4.2) in a covered beaker. Add, by small portions, a mixture of 25 ml of water and 20 ml of nitric acid (4.10). Heat gently. After dissolution is completed, boil to expel nitrous fumes. Allow to cool. Dilute to about 700 ml with water. Bring to pH 5,5 (using a pH-meter) by adding the hexamethylene tetramine solution (4.20). Transfer to a 1 000 ml volumetric flask, fill up with water nearly to the mark, mix and cool to room temperature, then fill up exactly to the mark and mix again.

NOTE 3 This solution is stable for several months.

4.22.1.2 Standardization

Place 25 ml of (0,1 mol/l) EDTA solution (4.21) in a 600-ml beaker. Add 25 ml of potassium hydroxide (4.15).

Dilute to 350 ml with water. Add 0,3 ml of xylenol orange indicator (4.23) and 5 ml of ammonium acetate solution (4.19). Carry out the procedure as specified in 7.5.

Determine the calibration factor t between the EDTA and zinc in triplicate and calculate the factors t_1, t_2 and t_3 using the following equations

$$t_1 = \frac{V_{E_1}}{V_{Z_1}} \quad \ldots (1)$$

$$t_2 = \frac{V_{E_2}}{V_{Z_2}} \quad \ldots (2)$$

$$t_3 = \frac{V_{E_3}}{V_{Z_3}} \quad \ldots (3)$$

where

V_E is the volume of (0,1 mol/l) EDTA solution, in millilitres, poured into the beaker (25 ml);

V_Z is the volume of zinc standard solution, in millilitres, used for titration.

Calculate, to four significant figures, the mean factor, t. If the range of the values of t_1, t_2, t_3 exceeds 0,001 repeat the standardization.

4.22.2 EDTA Standard solution.

NOTE 4 Standardization blank. A blank titration should be carried out in parallel with the standardization using all the reagents specified in the standardization but omitting the lead metal.

Weigh, to the nearest 0,1 mg, three portions of 0,1 g to 0,8 g of lead metal (4.1) and place in separate nickel crucibles (5.3). Record the masses as m_1, m_2 and m_3.

NOTE 5 The mass of lead metal should match the expected mass of lead metal in the test portion.

Carry out the procedure as specified in 7.3, 7.4 and 7.5.

Calculate the calibration factors f_1, f_2 and f_3 between the EDTA solution and lead metal for each titration using the following equations:

$$f_1 = m_1/t(V_{B_1} - V_{Z_1}) \quad \ldots (4)$$

$$f_2 = m_2/t(V_{B_2} - V_{Z_2}) \quad \ldots (5)$$

$$f_3 = m_3/t(V_{B_3} - V_{Z_3}) \quad \ldots (6)$$

where

m_1, m_2, m_3 are the masses, in grams, of each test portion of lead;

t is the mean factor of correspondence between EDTA and zinc solution determined in 4.22.1.2;

V_B is the volume of titrated zinc solution, in millilitres, used to titrate excess EDTA solution for the standardization blank;

V_Z is the volume of titrated zinc solution, in millilitres, used to titrate excess EDTA for lead metal.

Calculate to four significant figures, the mean factor, f, for the EDTA. If the range of values of f_1, f_2, f_3 exceeds 0,000 02 g/ml repeat the standardization.

4.23 Xylenol orange indicator.

Dissolve 0,5 g of xylenol orange in 100 ml of water.

5 Apparatus

5.1 Ordinary laboratory equipment.

5.2 Volumetric glassware, of class A complying with ISO 385-1, ISO 648 and ISO 1042 and used in accordance with ISO 4787.

5.3 Nickel crucibles, of capacity 30 ml to 35 ml with lids.

5.4 Zirconium crucibles, of capacity 30 ml to 35 ml with lids.

5.5 Membrane filter — cellulose nitrate, diameter 30 mm to 50 mm, mesh size 0,45 µm to 0,65 µm.

5.6 Membrane filter, diameter 30 mm to 50 mm, mesh size 0,45 µm. Membrane to be insoluble in sodium hydroxide EDTA solution.

NOTE 6 PVC is considered suitable.

5.7 A vacuum filtration apparatus, consisting of a 30 mm to 50 mm diameter funnel, and a one-litre evacuated Buchner flask.

6 Sample

6.1 Test sample

Prepare an air-equilibrated test sample in accordance with ISO 9599.

NOTE 7 A test sample is not required if predried test portions are to be used (see annex A).

6.2 Test portion

Take multiple increments, extract a test portion from the test sample in such a manner that it is representative of the contents of the dish or tray. Weigh, to the nearest 0,1 mg, 1 g of test sample. At the same time as the test portion is weighed, weigh test portions for the determination of hygroscopic moisture in accordance with ISO 9599.

Alternatively, the method specified in annex A may be used to prepare predried test portions directly from the laboratory sample.

7 Procedure

7.1 Number of determinations

Carry out the determinations at least in duplicate and as far as possible under repeatability conditions, on each test sample.

NOTE 8 Repeatability conditions exist where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.

7.2 Blank test

Carry out a blank test in parallel with the analysis using all reagents specified in the determination but omitting the test portion. The purpose of the blank test in this method is to check the quality of the reagents. If a significant blank titration value is obtained as a result of the blank test, check all reagents and rectify the problem.

7.3 Dissolution of test portion

Mix the test portion with 2 g of sodium peroxide (4.3) in a nickel (5.3) or zirconium (5.4) crucible. Cover the mixture with 3 g of sodium peroxide.

Heat gently until fusion is achieved. Bring the temperature up to a dark red heat and maintain for 2 min to 3 min while stirring.

After cooling, place the crucible and its contents in a 600-ml beaker (tall form). Add approximately 125 ml of water. Cover the beaker with a watch-glass and allow to stand to dissolve the melt.

Remove the crucible and its lid from the beaker, and wash first with water then with the acid washing mixture (4.12).

Add 3 ml of hydrofluoric acid (4.8), cover, and boil for 10 min then add 20 ml of perchloric acid (4.5). Remove the watch-glass, heat to fumes of perchloric acid and continue fuming until a final volume of approximately 10 ml remains; cool.

7.4 Separation of lead

Add 50 ml of sulfuric acid (4.13) and heat until abundant sulfuric fumes and sulfuric acid is refluxing in the beaker. Allow to cool. Carefully add 250 ml of water, cool to room temperature and add 150 ml of ethanol (4.7).

Allow the lead sulfate precipitate to settle for 1 h to 2 h and then filter under vacuum conditions through a cellulose nitrate membrane (5.5).

Rinse the beaker two or three times with washing solution (4.14). Wash the filter and filtration apparatus twice with washing solution (4.14). Evacuate under suction to ensure complete drainage.

Transfer the filter and precipitate into the original beaker. Clean the filter funnel with a piece of wetted filter paper and put the paper in the beaker.

In the following order add:

— 50 ml of sulfuric acid (4.9);

— 2 ml of perchloric acid (4.5) and

— 5 ml of nitric acid (4.10).

Cover the beaker with a watch-glass and heat to abundant sulfuric fumes.

Allow to cool. Carefully add 20 ml of water. Boil and continue heating until sulfuric acid is refluxing in the beaker.

NOTE 9 Less dense perchloric acid fumes may appear first and then, after evaporation of all perchloric acid, denser sulfuric acid fumes appear.

Stirring thoroughly, add 100 ml of cold water and later 50 ml of hot water. Re-cover the beaker with the watch-glass and boil gently for 5 min. Cool to room temperature. Add 100 ml of ethanol (4.7).

Cool again and allow to stand for 1 h.

Filter the reprecipitated lead sulfate under vacuum conditions through a membrane filter (5.6) previously wetted with some ethanol (4.7).

Wash the beaker two or three times with washing solution (4.14). Wash the filter and filtration apparatus in the same way and evacuate until the precipitate is almost dry.

Transfer the filter and precipitate into the original beaker.

Remove any trace of lead sulfate from the filter funnel using a covered stirring rod.

NOTE 10 A PVC filter or suitable alternative is to be used because cellulose filters would be dissolved under the test conditions in the next step and might induce coloured interferences during titration.

While stirring add 25 ml of the potassium hydroxide solution (4.15) and EDTA solution (4.21) according to table 1.

Table 1 — Volume of EDTA solution

Lead content % (*m/m*)	Volume of EDTA solution ml
10 to 60	50,00
60 to 80	70,00

Cover the beaker with the watch-glass and boil the solution gently until the precipitate is dissolved. Remove the filter and wash it with water.

Dilute to about 170 ml with water. Add 3 to 4 drops of xylenol orange indicator (4.23) and diluted nitric acid (4.16) until the colour changes to yellow (approximately 10 ml is needed).

NOTES

11 If barium is present, it may precipitate as barium sulfate.

12 If the bismuth content is less than 0,05 % (*m/m*), the following steps may be omitted.

Add 5 ml of zirconium nitrate solution (4.17) and, drop by drop, 5 ml of potassium hydroxide solution (4.15).

Boil the solution for approximately 5 min and allow to stand for 30 min while keeping warm.

NOTE 13 The barium sulfate precipitated above is dissolved again during this operation.

Cool the solution to room temperature and filter under vacuum conditions through a membrane filter (5.6) wetted with ethanol (4.7) and quantitatively collect the filtrate.

Wash the beaker at least five times with basic washing solution (4.18) and pour the solution through the filter. Wash the filter and filtration funnel again three times using basic washing solution (4.18).

Quantitatively transfer the filtrate to a 600-ml beaker.

Dropwise, add diluted nitric acid (4.16) until the colour of the solution changes to yellow.

NOTE 14 Barium sulfate may then be precipitated but does not retain lead sulfate as inclusions in the given operating conditions.

7.5 Titration

Add 2 g to 3 g of sodium fluoride (4.4) to the solution and boil thoroughly for 3 min with the beaker covered with a watch-glass after introduction of a glass rod.

Dilute to 350 ml with water. Cool to room temperature and add 5 ml of ammonium acetate solution (4.19).

Bring the solution pH to 5,5 ± 0,1 (using a pH-meter) with diluted nitric acid (4.16) or hexamethylene tetramine solution (4.20).

Stirring continuously, titrate with the zinc standard solution (4.22.1) until the colour of the solution clearly changes to red.

8 Expression of results

The lead content of the test portion w_{Pb}, expressed as a percentage by mass, is given by the following equation:

$$w_{Pb} = [(V_1 - tV_2) - (V_1 - tV_0)] \times f \times 100 \times \frac{100}{100 - H}$$

i.e.

$$w_{Pb} = t(V_0 - V_2) \times f \times 100 \times \frac{100}{100 - H} \quad \ldots (7)$$

where

V_0 is the volume of zinc standard solution in millilitres, used to titrate excess EDTA in the blank solution;

V_1 is the volume of 0,1 M EDTA solution, in millilitres, used in the sample and blank titrations;

V_2 is the volume of zinc standard solution, in millilitres, used to titrate excess EDTA in the sample solution;

t is the factor determined in 4.22.1.2;

f is the factor, in grams per millilitres, determined in 4.22.2;

H is the hygroscopic moisture content, as a percentage of the test portion (in the case of a predried test portion being used $H = 0$).

Calculate the lead content of the test portion to the second decimal place.

9 Precision

9.1 Expression of precision

The precision of this analytical method is expressed by the following equations:

$$s_r = 0{,}001\overline{X} + 0{,}079\ 0 \quad \ldots (8)$$

$$s_L = 0{,}002\overline{X} + 0{,}049\ 4 \quad \ldots (9)$$

where

$\overline{X}$ is the mean content of lead, expressed as a percentage by mass, in the sample;

s_r is the within-laboratory standard deviation, expressed as a percentage by mass of lead;

s_L is the between-laboratories standard deviation, expressed as a percentage by mass of lead.

NOTE 15 Additional information is given in annex C.

9.2 Method for obtaining the final result (see annex B)

Calculate the following quantities from the duplicate results X_1 and X_2 and process according to the flow chart in annex B:

Mean of duplicates

$$\overline{X} = (X_1 + X_2)/2 \quad \ldots (10)$$

Within-laboratory standard deviation

$$s_r = 0{,}001\overline{X} + 0{,}079\ 0 \quad \ldots (11)$$

Repeatability limit

$$r = 2{,}8 s_r \quad \ldots (12)$$

9.3 Precision between laboratories

The precision between laboratories is used to determine the agreement between the results reported by two (or more) laboratories. It is assumed that all laboratories have followed the same procedure.

Calculate the following quantities:

Mean of final results

$$\mu_{1,2} = (\mu_1 + \mu_2)/2 \quad \ldots (13)$$

Between-laboratories standard deviation

$$s_L = 0{,}002\mu_{1,2} + 0{,}049\ 4 \quad \ldots (14)$$

Within-laboratory standard deviation

$$s_r = 0{,}001\mu_{1,2} + 0{,}079\ 0 \quad \ldots (15)$$

Permissible difference

$$P = 2{,}8\sqrt{s_L^2 + \left(s_r^2/2\right)} \quad \ldots (16)$$

Range

$$E = |\mu_1 - \mu_2| \quad \ldots (17)$$

where

μ_1 is the final result, expressed as a percentage by mass of lead, reported by laboratory 1;

μ_2 is the final result, expressed as a percentage by mass of lead, reported by laboratory 2.

If E is equal to or less than P, the final results are in agreement.

9.4 Check of trueness

The trueness of the analytical method can be checked by applying it to a certified reference material (CRM). The procedure is the same as that described in 7. When the precision has been confirmed, the final laboratory result can be compared with the certified value, A_c.

The following two possibilities exist:

$$|\mu_c - A_c| \leqslant C \quad \ldots (18)$$

If this condition exists, the difference between the reported result and the certified value is statistically insignificant.

$$|\mu_c - A_c| > C \quad \ldots (19)$$

If this condition exists, the difference between the reported result and the certified value is statistically significant.

In equations (18) and (19), the symbols are defined as follows:

μ_c is the final result, as a percentage of lead mass of the certified reference material;

A_c is the certified value, as a percentage of lead mass of the certified reference material;

C is a quantity, expressed as a percentage of lead mass, depending on the type of the certified reference material used as defined in 9.4.1.

9.4.1 Type of certified reference material (CRM) or reference material (RM)

The reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35.

9.4.1.1 Reference material certified/characterized by an interlaboratory test programme

The quantity C (see 9.4), expressed as a percentage by mass of lead, is given by the following equation:

$$C = 2\sqrt{s_L^2 + \left(s_r^2/n\right) + s^2\{A_c\}} \quad \ldots (20)$$

where

$s^2\{A_c\}$ is the variance of the certified value;

n is the number of replicate determinations.

9.4.1.2 Reference material certified/characterized by one laboratory

The quantity C (see 9.4), expressed as a percentage by mass of lead, is given by the following equation:

$$C = 2\sqrt{2s_L^2 + \left(s_r^2/n\right)} \quad \ldots (21)$$

NOTE 16 It is recommended that this type of certified reference material be avoided, unless the particular CRM is known to have an unbiased certified value.

10 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) reference to this International Standard, i.e ISO 11441;

c) lead content of the sample, expressed as a percentage by mass;

d) date on which the test was carried out;

e) any occurrence noticed during the determination that may have had an influence on the results.

Annex A
(normative)

Procedure for the preparation and determination of the mass of a predried test portion

A.1 Scope

This annex specifies a method for the preparation and determination of the mass of a predried test portion in the analysis of lead sulfide concentrates.

The method is applicable to lead sulfide concentrates not susceptible to oxidation and with hygroscopic moisture contents ranging from 0,05 % to 2 %.

A.2 Principle

The test portion to be used for analysis is dried in air in an oven maintained at 105 °C ± 5 °C. The dried test portion is then weighed and used for the analysis. No correction for moisture is required.

A.3 Chemicals

A.3.1 Desiccant, such as self-indicating silica gel or anhydrous magnesium perchlorate.

WARNING — Care must be taken when disposing of exhausted magnesium perchlorate. It must be washed down the sink with a stream of running water.

A.4 Apparatus

Ordinary laboratory equipment, and

A.4.1 Analytical balance, sensitive to 0,1 mg.

A.4.2 Weighing vessels, of glass or silica or corrosion-resistant metal, with externally fitting air-tight covers. For small test portions of mass (less than 3 g), the mass of the vessel shall be as small as possible, i.e less than 20 g.

A.4.3 Laboratory oven, capable of maintaining a temperature of 105 °C ± 5 °C.

A.5 Procedure

A.5.1 Preparation of the weighing vessel

Dry the weighing vessel and vessel cover (A.4.2) by heating in the laboratory oven (A.4.3) at 105 °C ± 5 °C for 1 h. Transfer the vessel and its cover to a desiccator containing a suitable fresh desiccant (A.3.1) and allow to cool to ambient temperature.

A.5.2 Test portion

Determine the tare weight of the dried vessel and its cover (A.5.1). Immediately add the mass of laboratory sample specified for analysis. An accurate total mass of the test portion and weighing vessel is not required at this point.

A.5.3 Determination of the test portion dry mass

Transfer the uncovered weighing vessel containing the test portion and the vessel cover to the laboratory oven (A.4.3) and dry at 105 °C ± 5 °C for 2 h. After the 2-h period, remove the weighing vessel and dry test portion from the oven, replace the vessel cover and allow to cool to ambient temperature in the desiccator. When cool, remove the weighing vessel containing the dry test portion and the vessel cover from the desiccator and weigh to the nearest 0,1 mg (m_4) after slightly lifting the cover and quickly replacing it.

Transfer the test portion to the appropriate analytical apparatus and immediately reweigh the empty weighing vessel and its cover. Record the mass (m_5) to the nearest 0,1 mg.

NOTE 17 For new concentrates of unknown characteristics it is advisable to repeat the drying for another 2 h at 105 °C ± 5 °C and to reweigh the weighing vessel containing the test portion and the vessel cover to the nearest 0,1 mg (m'_4). The mass of the test portion can be considered to be constant if the difference, ($m_4 - m'_4$) is less

than or equal to 0,5 mg. If this condition is not achieved, the drying and weighing steps should be repeated.

A.6 Calculation of the test portion dry mass

The dry mass of the test portion m_6, in grams, is given by the following equation:

$$m_6 = m_4 - m_5 \quad \ldots (A.1)$$

where

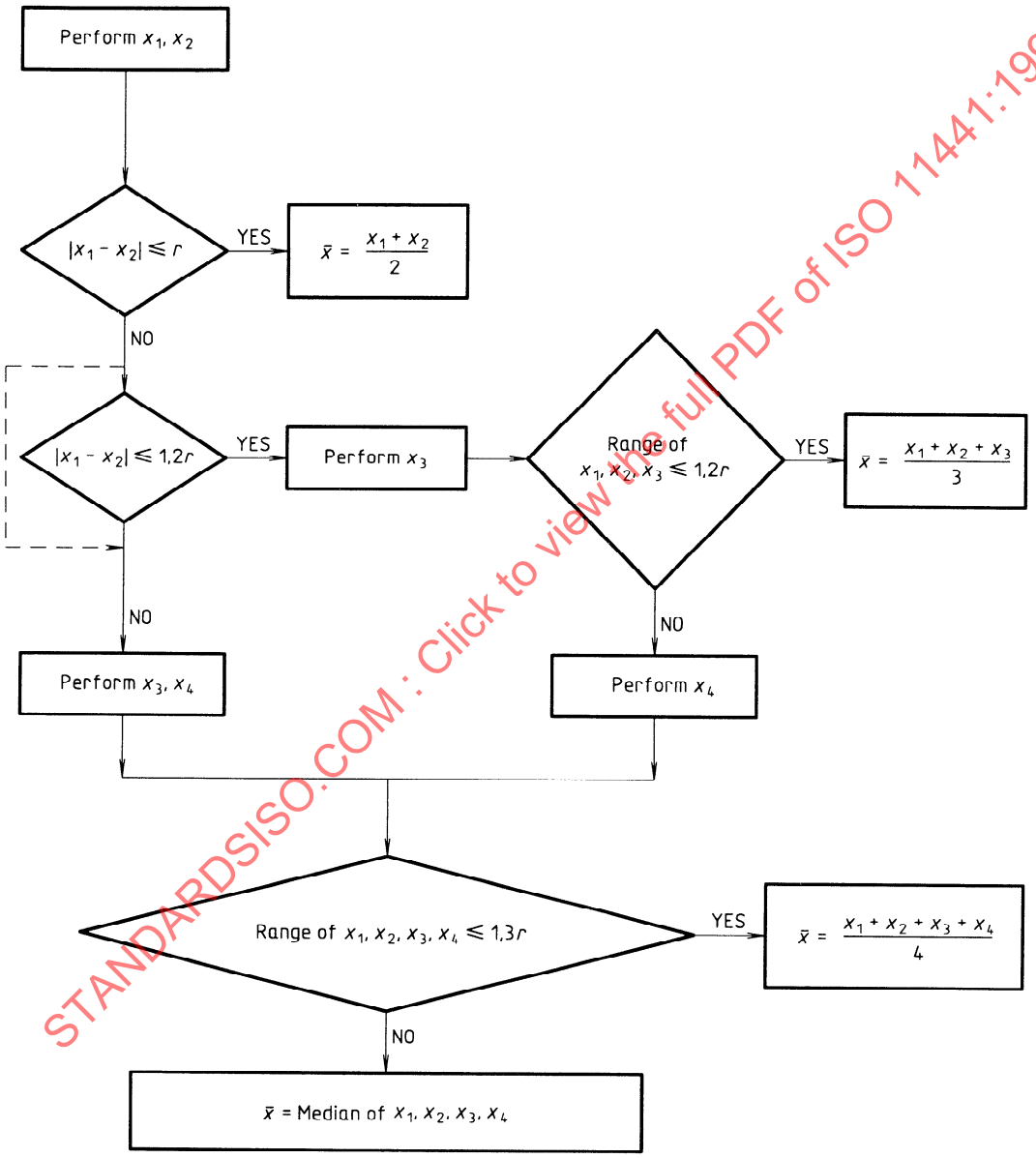
m_4 is the mass, in grams, of the dried test portion plus the weighing vessel and its cover;

m_5 is the mass, in grams, of the empty weighing vessel plus its cover.

The mass of the dry test portion is the mass to be used to calculate the element content in the laboratory sample on a dry basis. No correction for hygroscopic moisture is required.

Annex B
(normative)

Flow sheet of the procedure for the acceptance of analytical values for test samples



r : defined in 9.2

Annex C
(informative)

Derivation of precision equations

C.1 Introduction

This International Standard was tested in an interlaboratory test programme involving seven countries and twelve laboratories. Five samples of lead concentrate covering the range 13 % (*m/m*) to 74 % (*m/m*) were analysed to determine the lead content. The test programme was designed to determine the repeatability and within-laboratory and between-laboratories reproducibilities in general, using the principle of ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests*.

C.2 Design of the test programme

The analytical test programme was designed with the aim of providing maximum information. Each laboratory used two samples (two bags) of each concentrate and each sample was analyzed twice independently.

C.3 Test samples

This test programme used five samples of lead concentrate. The composition of these samples is shown in table C.1.

C.4 Statistical evaluation

The procedure for statistical evaluation is illustrated schematically in figure C.1. The results of the statistical evaluation are summarized in table C.2.

The estimated precisions (s_r, s_L, r and P) are plotted against their corresponding sample means on a graph as shown in figure C.2, and the regression equations of these precisions against sample means were computed and are presented in table C.2.

Table C.1 — Composition of lead concentrate samples

Element or compound	Unit	Sample numbers				
		89-4	**89-5**	**89-6**	**89-7**	**89-9**
Cu	% (*m/m*)	0,6	1,4	0,2	0,1	0,8
Pb	% (*m/m*)	70	65	50	30	20
Zn	% (*m/m*)	4,7	4,0	4,6	9,5	9,8
Au	g/t	0,7	1,4	—	0,2	15
Ag	g/t	1 290	540	1 310	900	8 940
S	% (*m/m*)	16,1	15,9	21,7	11,2	8,3
As	% (*m/m*)	0,04	0,1	0,04	0,07	0,3
Sb	% (*m/m*)	0,24	0,13	0,14	0,08	0,1
Sn	% (*m/m*)	0,02	0,02	0,01	0,01	0,02
Bi	% (*m/m*)	< 0,005	0,02	< 0,005	< 0,005	< 0,005
Fe	% (*m/m*)	1,8	3,9	13,0	13,9	11,4
SiO_2	% (*m/m*)	1,8	1,6	1,6	9,0	25,3
Al_2O_3	% (*m/m*)	0,5	0,3	0,4	3,0	9,9
CaO	% (*m/m*)	0,2	0,2	0,2	4,1	0,6
MgO	% (*m/m*)	0,23	0,14	0,4	0,58	0,32
Co	% (*m/m*)	0,014	0,018	0,018	0,027	0,016
Ni	% (*m/m*)	0,017	0,014	0,013	0,011	0,014
Cd	% (*m/m*)	0,023	0,016	0,016	0,127	0,055
Se	g/t	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005

89-4 North Broken Hill (Australia)

89-5 ZC Mines (Australia)

89-6 MIM (Australia)

89-7 MMM (Australia)

89-9 MMM (Australia)