INTERNATIONAL STANDARD

# ISO 10378

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# Copper, lead and zinc sulfide concentrates — Determination of gold and silver — Fire assay gravimetric and flame atomic absorption spectrometric method

*Concentrés de sulfure de cuivre, de plomb et de zinc — Dosage de l'or et de l'argent — Méthode gravimétrique par essai au feu et spectrométrie d'absorption atomique dans la flamme*

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# Foreword

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The committee responsible for this document is ISO/TC 183, *Copper, lead, zinc and nickel ores and concentrates*.

This third edition cancels and replaces the second edition (ISO 10378:2005), in which 6.2 has been technically revised and the warning notice in A.3.1 has been updated.

# Introduction

This International Standard describes a method for the determination of the mass fraction of gold and silver in copper, lead, and zinc sulfide concentrates. This International Standard was prepared to enable laboratories to determine the mass fraction of gold and silver in suitable samples using instrumental methods.

# Copper, lead and zinc sulfide concentrates — Determination of gold and silver — Fire assay gravimetric and flame atomic absorption spectrometric method

**WARNING — This International Standard may involve hazardous materials, operations, and equipment. It is the responsibility of the user of this International Standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.**

## 1 Scope

This International Standard specifies a fire assay gravimetric and flame atomic absorption spectrometric method for the determination of the mass fraction of gold and silver in copper, lead, and zinc sulfide concentrates as follows.

- Copper concentrates

  The method is applicable to the determination of mass fractions of gold from 0,5 g/t to 300 g/t and of mass fractions of silver from 25 g/t to 1 500 g/t in copper sulfide concentrates containing mass fractions of copper from 15 % to 60 %.

- Lead concentrates

  The method is applicable to the determination of mass fractions of gold from 0,1 g/t to 25 g/t and of mass fractions of silver from 200 g/t to 3 500 g/t in lead sulfide concentrates containing mass fractions of lead from 10 % to 80 %.

- Zinc concentrates

  The method is applicable to the determination of mass fractions of gold from 0,1 g/t to 12 g/t and of mass fractions of silver from 10 g/t to 800 g/t in zinc sulfide concentrates containing mass fractions of zinc up to 60 %.

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

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

# 3 Principle

## 3.1 General

Fire assaying for the determination of gold and silver comprises a series of steps to separate firstly the precious metals from most of the associated metals, followed by separation of the gold from silver and other metals pre-concentrated into a precious-metal alloy.

The stages that comprise the determinations are described in 3.2 to 3.6 inclusive.

## 3.2 Fusion

The samples are fused in a crucible after mixing with a litharge-based flux which, under reducing conditions, collects the precious metals in a metallic lead button.

## 3.3 Cupellation

The base metals present in the lead button are substantially separated from the precious metals by oxidizing fusion. Cupellation produces a bead largely comprising a silver-gold alloy with small quantities of other metals.

## 3.4 Parting

Gold is separated from the primary bead by treatment with nitric acid. The gold prill is weighed. Gold prills having a mass less than 50 µg are dissolved in aqua regia and the gold is determined by atomic absorption spectrometry (AAS). Silver is determined in the parting solution by AAS.

## 3.5 Retreatment

All residues are retreated to maximize the recovery of gold and silver. The addition of collectors for either gold or silver is not required, as both metals are present in sufficient amounts to be readily visible after the cupellation stage. The second bead is dissolved in acids followed by analysis of both metals by AAS.

## 3.6 Correction for blank contamination

Contamination by gold and silver impurities in the reagents is corrected for by fusing the reagents without the test portion.

# 4 Reagents

During the analysis, use only reagents of recognized analytical grade and water that complies with grade 2 of ISO 3696.

**4.1 Sodium carbonate**, anhydrous.

**4.2 Litharge** (PbO), assay grade having a mass fraction of gold of less than 0,01 g/t and a mass fraction of silver of less than 0,2 g/t.

**4.3 Silica**, precipitated.

### 4.4 Potassium nitrate or sodium nitrate

NOTE If sodium nitrate is used, the masses specified for potassium nitrate will have to be modified:

$$\text{g of KNO}_3 \times \frac{85{,}0}{101{,}1} = \text{g of NaNO}_3$$

### 4.5 Flour

**4.6 Borax**, fused anhydrous sodium tetraborate (borax glass powder).

**4.7 Nitric acid**, concentrated ($\rho_{20}$ 1,42 g/ml), chloride concentration <0,5 µg/ml.

**4.8 Nitric acid**, diluted 1+1.

Slowly add 500 ml of concentrated nitric acid (4.7) to 500 ml of water, while stirring.

**4.9 Lead**, foil, having a mass fraction of gold of less than 0,01 g/t and a mass fraction of silver of less than 0,2 g/t.

**4.10 Silver**, of minimum purity 99,99 %.

**4.11 Hydrochloric acid** ($\rho_{20}$ 1,16 g/ml to 1,19 g/ml).

**4.12 Thiourea**, 10 g/l solution.

Add 1 g of thiourea to 100 ml of water.

### 4.13 Aqua regia

Mix three parts of hydrochloric acid (4.11) with one part of nitric acid (4.7). Prepare freshly as required.

### 4.14 Standard solutions

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

**4.14.1 Silver**, standard stock solution A (500 µg of Ag/ml).

Weigh 0,500 0 g of silver metal to the nearest 0,1 mg. Transfer to a 100 ml beaker, add 20 ml of diluted nitric acid (4.8), and warm to dissolve. Cool and add 20 ml of concentrated nitric acid (4.7). 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.

**4.14.2 Silver**, standard solution B (50 µg of Ag/ml).

Pipette 10,00 ml of silver standard stock solution A (4.14.1) into a 100 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.

Prepare a fresh solution per batch.

**4.14.3 Gold**, standard solution (1 000 µg of Au/ml).

Weigh 1,000 g of gold metal to the nearest 0,1 mg. Transfer to a 200 ml beaker, add 25 ml of aqua regia solution (4.13), and warm to dissolve. Cool and transfer to a 1 000 ml volumetric flask. Add 75 ml of hydrochloric acid (4.11), fill up nearly to the mark with water, mix and cool to room temperature; then fill up exactly to the mark and mix again.

#### 4.14.4 Gold and silver, standard solution (100 µg of Au/ml + 50 µg of Ag/ml).

Pipette 10,00 ml of silver standard stock solution A (4.14.1) into a 100 ml volumetric flask. Add 40 ml of hydrochloric acid (4.11). Pipette 10,00 ml of gold standard solution (4.14.3) into the volumetric flask. Fill up nearly to the mark with water, mix and cool to room temperature; then fill up exactly to the mark and mix again.

### 4.15 Calibration solutions

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

#### 4.15.1 Gold/silver calibration solutions

Pipette 0,0 ml, 1,00 ml, 2,00 ml, 5,00 ml, and 10,00 ml of gold and silver standard solution (4.14.4) into a series of 100 ml one-mark volumetric flasks.

Add 40 ml of hydrochloric acid (4.11) to each flask, fill up nearly to the mark with water, mix and cool to room temperature; then fill up exactly to the mark and mix again.

These solutions contain 0,0 µg of Au/ml, 1,00 µg of Au/ml, 2,00 µg of Au/ml, 5,00 µg of Au/ml, and 10,00 µg of Au/ml; and 0,0 µg of Ag/ml, 0,50 µg of Ag/ml, 1,00 µg of Ag/ml, 2,50 µg of Ag/ml, and 5,00 µg of Ag/ml, and shall be freshly prepared.

#### 4.15.2 Silver calibration solutions

Pipette 0,0 ml, 1,00 ml, 2,00 ml, 4,00 ml, 6,00 ml, 8,00 m,l and 10,00 ml of silver standard solution B (4.14.2) into a series of 100 ml volumetric flasks. Add 10 ml of nitric acid (4.7), fill up nearly to the mark with water, mix and cool to room temperature; then fill up exactly to the mark and mix again.

These solutions contain 0,0 µg of Ag/ml, 0,50 µg of Ag/ml, 1,00 µg of Ag/ml, 2,00 µg of Ag/ml, 3,00 µg of Ag/ml, 4,00 µg of Ag/ml, and 5,00 µg of Ag/ml, and shall be freshly prepared.

Contamination by gold and silver impurities in the reagents is corrected for by fusing the reagents without the test portion.

## 5 Apparatus

**5.1 Assay crucible furnace**, with a maximum required operating temperature of 1 200 °C.

**5.2 Muffle furnace**, with a maximum required operating temperature of 1 100 °C. Temperature indication, automatic temperature control, and controlled air flow are preferable.

**5.3 Assay crucibles**, made of fire clay, of nominal capacity 200 ml to 600 ml, capable of withstanding corrosion by the samples and fluxes at 1 100 °C.

The crucible shall be of such a size that the charge does not fill the crucible to a depth greater than 3/4 the depth of the crucible.

**5.4 Cupels**, made of magnesium oxide, or bone-ash cupels having a nominal capacity of 50 g of molten lead.

The inside bottom of the cupel shall be concave, as recommended in the fire assay texts referred to in the Bibliography.

**5.5 Conical mould**, made of cast iron, of sufficient capacity to contain all of the molten lead plus slag from the crucible fusion.

**5.6 Analytical balance**, sensitive to 1 mg.

**5.7 Microbalance**, sensitive to 1 µg or less.

**5.8 Ordinary laboratory glassware**, washed free of chlorides.

**5.9 Volumetric glassware**, of class A complying with ISO 385, ISO 648, and ISO 1042, and used in accordance with ISO 4787.

**5.10 Atomic absorption spectrometer (AAS)**, equipped with background correction and a glass bead in the spray chamber.

**5.11 Inductively coupled plasma (ICP) atomic emission spectrometer**.

**5.12 Pulverizer**.

**5.13 Hotplate**.

## 6 Sample

### 6.1 Test sample

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

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

### 6.2 Test portion

Taking multiple increments, extract a test portion from the test sample in such a manner that it is representative of the whole contents of the dish or tray. Weigh to the nearest 1 mg approximately 10 g to 20 g of the test sample. At the same time as test portions are being weighed for analysis, weigh test portions for the determination of hygroscopic moisture in accordance with ISO 9599.

NOTE 1 The precision of determination of the mass of contained gold in a lot is the sum of sampling and analytical precision. The presence of particulate gold in a concentrate contributes to imprecision of the analytical component of total precision. When it has been established that the presence of particulate gold in a concentrate causes unacceptable imprecision, the following mixing and sampling methods are recommended.

a) Mix the sample by either of the following preferred mixing methods as described in ISO 12743:2006:

— 15.3.2 c), strip mixing;

— 15.3.2 e), riffle, or rotary divider.

*Mixing methods in items a), b), and d) in* ISO 12743:2006, 15.3.2 *are not recommended.*

b) Extract a test portion from the test sample using either of the following methods described in ISO 12743:2006:

— 15.4.1 a), rotary sample division;

— 15.4.1 f), ribbon division.

*Methods in items b) to e) and g) in* ISO 12743:2006, 15.4.1 *are not recommended*.

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

If a mass fraction of arsenic above 2 % is present in the sample, this element should be removed by following the procedure in Annex J; otherwise, interference with the cupellation stage may occur.

NOTE 2 If the mass fraction of copper is greater than 30 %, a 10 g or 15 g test portion is preferable (see the fourth paragraph of 7.4).

For lead concentrates, the test portion should be 10 g to ensure an adequate supply of lead.

# 7 Procedure

## 7.1 Number of determinations

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

NOTE 1 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.

NOTE 2 In the case where the ratio of silver to gold does not exceed 2,5 to 1 and the procedure specified in 7.10 is carried out for the silver determination, separate determinations for gold and silver will be necessary (see Annex D). Four test portions, therefore, are required, i.e. two for determinations of gold and two for silver.

NOTE 3 Annex I contains a flowsheet of the method.

## 7.2 Trial fusion

Carry out a trial fusion as described in Annex B, to ensure that the mass of the lead button is between 30 g and 45 g.

## 7.3 Blank tests

Carry out a reagent blank test as described in Annex C in parallel with the analysis, using the same quantities of all reagents, with the addition of sufficient flour (4.5) to the flux to give a lead button of between 30 g and 45 g. Omit the test portion and the potassium nitrate. The total blank should not exceed 5 µg of gold or 100 µg of silver.

## 7.4 Charge preparation

Determine the mass of potassium nitrate (4.4) and flour (4.5) required in the charge, as indicated by the trial fusion (see Annex B), and include this reagent in the flux mixture. Typical masses of the flux components for copper, lead, and zinc concentrates are shown in Tables 1 to 3 respectively.

Thoroughly mix the test portion with a flux.

Intimate mixing of flux components and the test portion is very important. All flux components should be in a finely divided state with a preferred particle size of less than 0,5 mm.

**Table 1 — Typical masses of flux components for copper concentrates**

| Flux components | Mass<br>g |
|---|---|
| Sodium carbonate (4.1) | 30 |
| Litharge (4.2) | 210 |
| Silica (4.3) | 25 |
| Potassium nitrate (4.4) | — |
| Flour (4.5) | — |
| Test portion | 20 |

If the mass fraction of copper is greater than 30 %, the mass of litharge should be 30 times that of copper plus 35 g for the lead button. Alternatively, a 10 g or 15 g test portion can be used while retaining the flux composition given in Table 1. If there are difficulties experienced in achieving a fluid melt, the amount of silica recommended in Table 1 can be reduced to 19 g, while including 6 g borax.

**Table 2 — Typical masses of flux components for lead concentrates**

| Flux components | Mass, g |
|---|---|
| Sodium carbonate (4.1) | 30 |
| Litharge (4.2) | 100 |
| Silica (4.3) | 10 |
| Borax (4.6) | 10 |
| Potassium nitrate (4.4) | — |
| Flour (4.5) | — |
| Test portion | 10 |

**Table 3 — Typical masses of flux components for zinc concentrates**

| Flux components | Mass, g |
|---|---|
| Sodium carbonate (4.1) | 30 |
| Litharge (4.2) | 120 |
| Silica (4.3) | 10 |
| Borax (4.6) | 10 |
| Potassium nitrate (4.4) | — |
| Flour (4.5) | — |
| Test portion | 20 |

Place the mixture in an assay crucible (5.3).

## 7.5 Primary fusion

Place the crucibles in the furnace (5.1) preheated to approximately 900 °C.

If oil-fired or gas-fired furnaces are used, the fuel should be turned off immediately before opening the furnace.

Slowly raise the furnace temperature to 1 000 °C to 1 050 °C. Maintain this temperature until the fusion has been tranquil for at least 10 min.

The optimum furnace setting temperature depends on the furnace structure and the position of the thermometer. If unfused material remains in the bottom of assay crucibles, the setting temperature of the furnace should be raised and the assay repeated.

To minimize crucible corrosion and build-up of impurities in the lead button, the overall fusion time should not exceed 40 min. However, should the fusion take an extended time to settle, the fusion time may need to exceed 40 min.

It is recommended that a fire-clay lid or a layer of salt or borax approximately 12 mm thick be used with this fusion to prevent loss of material by dusting or ebullition. If borax is used as a cover, the amount used in the flux may be reduced accordingly. If some “shotting” of the lead is noted in the slag (this is common for zinc concentrates), it is recommended that the extra borax be retained.

Pour the mixture into a dry conical mould (5.5), taking care that no loss of lead or slag occurs. Reserve the crucible for retreatment fusion.

Allow the mixture to cool and carefully separate the lead button from the slag. Hammer the lead button as necessary to remove any small particles of adhering slag. Reserve the slag for retreatment.

Weigh the lead button. If the button weighs less than 30 g or more than 45 g, discard the button and slag and repeat the assay after appropriate adjustment of the oxidizing agent (see Annex B).

NOTE Buttons weighing less than 30 g may show poor collection efficiencies, whereas those exceeding 45 g may contain higher amounts of copper and other base metals.

## 7.6 Cupellation

Place the lead button obtained in 7.5 into a preheated cupel (5.4) in a muffle furnace (5.2) at 900 °C. Allow the cupellation to proceed at the lower muffle temperature of approximately 860 °C with a steady air flow.

Variations depend on the cupel type and furnace conditions. In the case of cupels made of bone ash, a cupellation temperature of 820 °C is recommended.

NOTE 1 In the case where only gold is being determined, it could be effective to raise the furnace temperature to 900 °C to finish the cupellation after the visible lead melt on the cupel is approximately 10 mm in diameter [approximately 80 % (mass fraction) of lead absorbed].

High cupellation temperatures will cause higher silver losses and low temperatures can cause “freezing” of the bead and incomplete cupellation. It is recommended that loss of silver during the cupellation process be determined, to decide upon the furnace conditions (see Annex E).

Remove the cupel from the furnace and cool.

Carefully extract the primary bead and remove any adhering cupel material with a brush. Flatten the bead slightly and place in a 30 ml porcelain crucible.

NOTE 2 A test tube can be used instead of a porcelain crucible.

NOTE 3 If the ratio of silver to gold in the primary bead is greater than 2,5 to 1, the silver can be determined by the gravimetric method instead of the procedure specified in 7.10. For the gravimetric method, weigh the primary bead, in micrograms, to the nearest 1 µg ($m_0$), carry out the parting by the procedure specified in 7.8, and determine the impurities in the parting solutions and washings by the procedure specified in Annex G.

NOTE 4 If it is difficult to recover the bead because of its small size, 1 mg of palladium can be added before fusion. In this case, the palladium bead is dissolved and determined by the procedure specified in 7.9.

Reserve the cupel for retreatment of residues.

## 7.7 Retreatment of residues

Place both the cupel and the slag in a pulverizer (5.12) and pulverize for about 20 s to reduce the material to minus 150 µm.

If magnesium cupels are used, it is recommended that the slag and the cupel be retreated separately.

NOTE 1 Longer grinding can cause caking of the material and heating of the grinding barrel.

NOTE 2 The pulverizer may be cleaned between samples by grinding small portions of broken glass or quartz.

Thoroughly mix the ground residues with a flux. Typical composition of the flux is shown in Table 4.

**Table 4 — Typical masses of flux components for the retreatment of residues**

| **Flux components** | **Mass**, g | |
|---|---|---|
| | **Magnesium oxide cupel** | **Bone ash cupel** |
| Sodium carbonate (4.1) | 50 to 60 | 40 |
| Litharge (4.2) | 50 to 60 | 45 |
| Silica (4.3) | 50 to 60 | 20 |
| Flour (4.4) | 4 | 2 to 3 |
| Borax (4.6) | 30 to 50 | 15 |

The mass of flour shown in Table 4 is typical. The mass should be sufficient to produce a 30 g to 45 g lead button.

The combined mass of slag and cupel of the primary fusion, in addition to the flux components given in Table 4, may exceed the capacity of the assay crucibles, or the re-fusion may be so reactive that the fusions may froth over. In these cases, it is permissible to split the residues into equal halves and fuse separately in two crucibles. The lead buttons obtained should be cupelled separately, or be scorified together and the resultant lead button cupelled.

Place the mixture in the original assay crucible.

Carry out the fusion as detailed in 7.5 and discard the crucible and slag.

Cupel the lead button as detailed in 7.6 to obtain a second bead and discard the cupel.

## 7.8 Determination of gold in the primary bead

Add 10 ml of dilute nitric acid (4.8) to the primary bead in the porcelain crucible prepared in 7.6 and heat gently on a hotplate (5.13) for 20 min or until the reaction ceases.

NOTE 1 It is essential that chloride be absent during parting; otherwise, some of the gold may dissolve.

When the bead is treated with hot dilute nitric acid, silver will start to dissolve provided that the ratio of silver to gold in the bead exceeds 2,5 to 1. The rate of dissolution increases with increasing mass fraction of silver of the bead. Rapid attack of the bead should be avoided by further dilution and slow heating to prevent disintegration of the gold. Should the ratio of silver to gold be less than 2,5 to 1, as shown by failure to part in hot dilute nitric acid, the bead should be inquarted (see Annex D).

If there is danger of the gold sponge crumbling during the parting operation, it is recommended that the operation be carried out with sulfuric acid (see Annex F).

Carefully pour the solution into a 200 ml beaker by decantation to avoid losses.

Add 15 ml of warm dilute nitric acid (4.8) to the porcelain crucible and continue heating gently until parting is complete. This should take approximately 25 min.

Carefully pour the solution into the 200 ml beaker by decantation to avoid losses. Wash the crucible and gold with four 15 ml volumes of hot water. Collect all the washings in the same 200 ml beaker. Reserve the solution for the determination of silver as specified in 7.10.

NOTE 2 The possibility of gold particles occurring in the collected parting and washing solutions can be determined by evaporating the solutions slowly down to 2 ml to 3 ml, then continuing with the determination as specified in 7.9.

Dry the gold sponge in the porcelain crucible on the hotplate.

Place the crucible in the muffle furnace (5.2) to anneal the gold at dull red heat for approximately 5 min.

Cool and weigh the resultant gold prill, in micrograms, to the nearest 1 µg ($m_1$).

If the mass of the gold is less than 50 µg, it is recommended that the gold be dissolved and determined by the procedure specified in 7.9.

If the mass of the gold is less than 50 µg, repeat the fusion and cupellation, then dissolve the prepared bead and determine the gold and silver concentration as specified in 7.9 without the parting operation. This alternative procedure is recommended where there is a danger of the gold sponge crumbling during the parting operation. The procedure, however, cannot be applied if the product of mass of test portion by mass fraction of silver, i.e. mass in test portion, is larger than 7 500 µg.

NOTE 3 If the sensitivity of the microbalance is 0,1 µg, the applicable range of the gravimetric method can be extended to 5 µg of gold. In such a case, weigh the gold prill, in micrograms, to the nearest 0,1 µg ($m_1$).

Reserve the gold prill to determine silver in the prill. The prill is dissolved and the silver concentration is determined as specified in 7.9. Several of the weighed prills of the same laboratory sample can be combined for the determination.

Platinum and palladium are removed from the prill during parting with nitric acid. If the determination of these elements remaining in the prill is considered necessary, determine these by the procedure specified in 7.9, followed by the addition of platinum and palladium to the standard solutions in relevant proportions. If a sufficient detection limit for AAS or ICP cannot be obtained on a single prill basis, a large number of prills of the same laboratory sample should be combined.

## 7.9 Determination of gold and silver in secondary beads and blanks, and of silver in prills

For blanks and samples determined by the procedure specified in the fourth last paragraph of 7.8 without the parting operation, the primary and secondary beads should be combined and treated together.

Transfer the bead(s) or prill(s) to a test tube or a porcelain crucible. Add 2 ml of nitric acid (4.7) and warm in a heating block or a sand bath set at approximately 98 °C. Add 6 ml of hydrochloric acid (4.11) and heat again to dissolve the gold. If necessary, add a further 2 ml of nitric acid (4.7). Take the above solution, or that prepared according to Annex C, and heat almost to dryness.

The solution should not be allowed to evaporate to dryness; otherwise, metallic gold will form.

Remove the test tube or the crucible from the heating block or the sand bath and allow cooling. Add 10 ml of hydrochloric acid (4.11) and mix or swirl to dissolve any salts. Transfer quantitatively to a 50 ml volumetric flask, add 10 ml of hydrochloric acid (4.11), make up to the mark with water, and mix well.

Depending upon the mass fraction of silver (see Annex K), it may be necessary to make dilutions so that the concentration of silver in the test solutions is in the range covered by the silver calibration solutions (4.15.1). Hydrochloric acid (4.11) should be added so that 40 ml of the acid is contained per 100 ml of the diluted test solutions.

Aspirate the test solutions and gold/silver calibration solutions (4.15.1) into the atomic absorption spectrometer (5.10) and measure the absorbance. As a guide, the atomic absorption settings shown in Table 5 are recommended; however, the instrument should be optimized to be free from any interference and to give maximum sensitivity and as near as practical to a linear relationship between absorbance and concentration.

**Table 5 — Recommended atomic absorption settings**

| Parameter | Gold | Silver |
|---|---|---|
| Flame | air/acetylene (oxidizing) | |
| Wavelength | 242,8 nm | 328,1 nm |
| Lamp current | 4 mA | 5 mA |
| Background corrector | on | off |
| Aspiration rate | optimize for maximum signal | |
| Integration time | 3 s | |
| Number of integrations | 5 | |
| Absorbance of 5 µg/ml calibration solution | 0,17 | 0,55 |

Perform three measurements on each test solution and calibration solution. Calculate, to three significant figures, the mean absorbance for each solution, provided that the range of values does not exceed 0,003 absorbance units. If this range is exceeded, repeat the measurement.

In order to clean out the nebulizer system, it is recommended to aspirate a cleaning solution, which is, for instance, prepared by carefully adding 500 ml of hydrochloric acid (4.11) and 100 ml of concentrated nitric acid (4.7) to 400 ml of water, between measurements.

Plot a calibration graph of absorbance versus concentration and determine the gold and/or silver concentrations, in micrograms per millilitre, in the test solutions, followed by calculation of the mass ($m_a$), in micrograms, of the gold and/or silver using Formula (1):

$$m_a = \rho \times \mathrm{TDF} \qquad (1)$$

where

$\rho$ is the mass concentration of gold and/or silver;

TDF is the total dilution factor.

Alternatively, an ICP atomic emission spectrometer (5.11) can be used for the determination of gold and silver at the appropriate wavelength. Typical wavelengths are 242,8 nm for gold and 328,1 nm for silver; however, the instrument should be optimized to be free from any interference and to give maximum sensitivity and as near as practical to a linear relationship between absorbance and concentration. In order to improve the precision, it is recommended that a simultaneous internal standard correction be adopted. Yttrium is generally used as an internal standard.

During all AAS or ICP determinations, the test solutions and calibration solutions should have the same temperature, as well as the same acid concentration.

## 7.10 Determination of silver in the parting solution

NOTE 1 This determination is applicable where the ratio of silver to gold is greater than 2,5 to 1 and the silver has been parted from the gold as indicated in 7.8.

NOTE 2 The silver can be determined by the gravimetric method instead of the procedure specified in this subclause. For the gravimetric method, determine the impurities in the parting solutions and washings by the procedure specified in Annex G.

Take the parting solutions and washings, which were reserved in 7.8. Heat to evaporate to approximately 20 ml, cool, and then add 2 ml of nitric acid (4.8). Transfer quantitatively to a 100 ml volumetric flask, make up to the mark with water, and mix well.

If the solution turns cloudy, add 1 % of thiourea solution (4.12) drop by drop, while stirring until the solution is clear. Add 2 ml in excess, then dilute to volume.

Depending upon the mass fraction of silver (see Annex K), it may be necessary to make dilutions so that the concentration of silver in the test solutions is in the range covered by silver calibration solutions (4.15.2). Nitric acid (4.7) should be added so that 10 ml of the acid is contained per 100 ml of the diluted test solutions.

Aspirate the test solutions and silver calibration solutions (4.15.2) into the atomic absorption spectrometer (5.10) and measure the absorbance. As a guide, the atomic absorption settings shown in Table 5 are recommended; however, the instrument should be optimized to be free from any interference and to give maximum sensitivity, and as near as practical to a linear relationship between absorbance and concentration.

Perform three measurements on each test solution and calibration solution. Calculate, to three significant figures, the mean absorbance for each solution, provided that the range of values does not exceed 0,003 absorbance units. If this range is exceeded, repeat the measurement.

Plot a calibration graph of absorbance versus concentration and determine the silver concentrations, in micrograms per millilitre, in the test solutions, followed by calculation of the mass ($m_a$), in micrograms, of the silver using Formula (1).

Alternatively, an ICP atomic emission spectrometer (5.11) can be used for the determination of silver at the appropriate wavelength. A typical wavelength is 328,1 nm; however, the instrument should be optimized to be free from any interference and to give maximum sensitivity and as near as practical to a linear relationship between absorbance and concentration. In order to improve the precision, it is recommended that a simultaneous internal standard correction be adopted. Yttrium is generally used as an internal standard.

During all AAS or ICP determinations, the test solutions and calibration solutions should have the same temperature, as well as the same acid concentration.

# 8 Expression of results

## 8.1 Mass fraction of gold

The mass fraction of gold of the test portion ($w_{Au}$), expressed in grams per tonne, is given by Formula (2):

$$w_{Au} = \frac{m_1 + m_2 - (m_B + m_{BR}) - m_5 + m_W}{m} \times \frac{100}{100 - H} \qquad (2)$$

where

| | |
|---|---|
| $m_1$ | is the mass, in micrograms, of gold obtained in the primary bead (as weighed or as determined by AAS); |
| $m_2$ | is the mass, in micrograms, of gold in the secondary bead; |
| $m_B + m_{BR}$ | is the mass, in micrograms, of gold in the primary blank bead combined with the mass of gold in the secondary blank bead; |
| $m_5$ | is the mass, in micrograms, of silver remaining in the prill (in the case of AAS being used to obtain $m_1$, $m_5 = 0$); |
| $m_W$ | is the mass, in micrograms, of gold in the parting and washing solutions; |
| $m$ | is the mass, in grams, of the test portion; |
| $H$ | is the hygroscopic moisture content, in percent, of the test portion (in the case of a pre-dried test portion being used, $H = 0$). |

## 8.2 Mass fraction of silver

If the silver is determined by the procedure specified in 7.10, the mass fraction of silver of the test portion ($w_{Ag}$), expressed in grams per tonne, is given by Formula (3):

$$w_{\mathrm{Ag}} = \frac{m_3 + m_4 - (m_{\mathrm{B}} + m_{\mathrm{BR}}) + m_5}{m} \times \frac{100}{100 - H} \tag{3}$$

where

| | |
|---|---|
| $m_3$ | is the mass, in micrograms, of silver in the parting and washing solutions; |
| $m_4$ | is the mass, in micrograms, of silver in the residue recovered; |
| $m_B + m_{BR}$ | is the mass, in micrograms, of silver in the blank primary bead combined with the mass of silver in the blank determination of the residue recovered; |
| $m_5$ | is the mass, in micrograms, of silver remaining in the prill; |
| $m$ | is the mass, in grams, of the test portion; |
| $H$ | is the hygroscopic moisture content, in percent, of the test portion (in the case of a pre-dried test portion being used, $H = 0$). |

If complete recovery of silver during the cupellation process is not obtained, correct the mass fraction of silver of the test portion (see Annex E).

If the silver is determined by the gravimetric method instead of the procedure specified in 7.10, the mass fraction of silver of the test portion ($w_{Ag}$), expressed in grams per tonne, is given by Formula (4):

$$w_{\mathrm{Ag}} = \frac{m_0 - m_1 + m_4 - (m_{\mathrm{B}} + m_{\mathrm{BR}}) + m_5 - m_{\mathrm{imp}}}{m} \times \frac{100}{100 - H} \tag{4}$$

where

| | |
|---|---|
| $m_0$ | is the mass, in micrograms, of the primary bead; |
| $m_1$ | is the mass, in micrograms, of gold obtained in the primary bead (as weighed or as determined by AAS); |
| $m_4$ | is the mass, in micrograms, of silver in the residue recovered; |
| $m_B + m_{BR}$ | is the mass, in micrograms, of silver in the blank primary bead combined with the mass of silver in the blank determination of the residue recovered; |
| $m_5$ | is the mass, in micrograms, of silver remaining in the prill; |
| $m_{imp}$ | is the total mass, in micrograms, of impurities in the parting and washing solutions obtained by the procedure specified in Annex G; |
| $m$ | is the mass, in grams, of the test portion; |
| $H$ | is the hygroscopic moisture content, in percent, of the test portion (in the case of a pre-dried test portion being used, $H = 0$). |

If complete recovery of silver during the cupellation process is not obtained, correct the mass fraction of silver of the test portion (see Annex E).

# 9 Precision

## 9.1 Expression of precision

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

**Zinc concentrates**

**Gold**

$$S_r = 0{,}022\,5\,\overline{X} + 0{,}032\,5 \quad (5)$$

$$S_L = 0{,}050\,4\,\overline{X} + 0{,}057\,1 \quad (6)$$

**Silver**

$$S_r = 0{,}009\,1\,\overline{X} + 2{,}057\,5 \quad (7)$$

$$S_L = 0{,}016\,6\,\overline{X} + 5{,}775\,0 \quad (8)$$

**Lead concentrates**

**Gold**

$$S_r = 0{,}030\,9\,\overline{X} + 0{,}033\,6 \quad (9)$$

$$S_L = 0{,}058\,2\,\overline{X} + 0{,}055\,3 \quad (10)$$

**Silver**

$$S_r = 0{,}003\,2\,\overline{X} + 5{,}843\,8 \quad (11)$$

$$S_L = 0{,}003\,2\,\overline{X} + 16{,}974\,7 \quad (12)$$

**Copper concentrates**

**Gold**

$$S_r = 0{,}004\,4\,\overline{X} + 0{,}242\,2 \quad (13)$$

$$S_L = 0{,}008\,4\,\overline{X} + 0{,}265\,1 \quad (14)$$

**Silver**

$$S_r = 0{,}007\,5\,\overline{X} + 0{,}968\,8 \quad (15)$$

$$S_L = 0{,}010\,9\,\overline{X} + 2{,}155\,8 \quad (16)$$

where

$\overline{X}$ is the mean mass fraction of gold or silver, in grams per tonne, in the sample;

$S_r$ is the within-laboratory standard deviation, in grams of gold or silver per tonne;

$S_L$ is the between-laboratories standard deviation, in grams of gold or silver per tonne.

NOTE Additional information is given in Annex L.

## 9.2 Method for obtaining the final result (see Annex H)

Calculate the following quantities from the duplicate results $X_1$ and $X_2$ and process according to the flowsheet in Annex H:

$$\text{Mean of duplicates } \bar{X} = \frac{X_1 + X_2}{2} \tag{17}$$

Within-laboratory standard deviation

**Zinc concentrates**

**Gold determination**

$$S_r = 0{,}022\,5\,\bar{X} + 0{,}032\,5 \tag{18}$$

**Silver determination**

$$S_r = 0{,}009\,1\,\bar{X} + 2{,}057\,5 \tag{19}$$

**Lead concentrates**

**Gold determination**

$$S_r = 0{,}030\,9\,\bar{X} + 0{,}033\,6 \tag{20}$$

**Silver determination**

$$S_r = 0{,}003\,2\,\bar{X} + 5{,}843\,8 \tag{21}$$

**Copper concentrates**

**Gold determination**

$$S_r = 0{,}004\,4\,\bar{X} + 0{,}242\,2 \tag{22}$$

**Silver determination**

$$S_r = 0{,}007\,5\,\bar{X} + 0{,}968\,8 \tag{23}$$

**Repeatability limit**

$$e = 2{,}8\,S_r \tag{24}$$

## 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 the laboratories followed the same procedure.

Calculate the following quantities:

Mean of final results

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \tag{25}$$

Between-laboratories standard deviation

**Zinc concentrates**

**Gold determination**

$$S_L = 0,0504\,\mu_{1,2} + 0,0571 \tag{26}$$

**Silver determination**

$$S_L = 0,0166\,\mu_{1,2} + 5,7750 \tag{27}$$

**Lead concentrates**

**Gold determination**

$$S_L = 0,0582\,\mu_{1,2} + 0,0553 \tag{28}$$

**Silver determination**

$$S_L = 0,0032\,\mu_{1,2} + 16,9747 \tag{29}$$

**Copper concentrates**

**Gold determination**

$$S_L = 0,0084\,\mu_{1,2} + 0,2651 \tag{30}$$

**Silver determination**

$$S_L = 0,0109\,\mu_{1,2} + 2,1558 \tag{31}$$

Within-laboratory standard deviation

**Zinc concentrates**

**Gold determination**

$$S_r = 0,0225\,\mu_{1,2} + 0,0325 \tag{32}$$

**Silver determination**

$$S_r = 0,0091\,\mu_{1,2} + 2,0575 \tag{33}$$

**Lead concentrates**

**Gold determination**

$$S_r = 0{,}030\,9\,\mu_{1,2} + 0{,}033\,6 \qquad (34)$$

**Silver determination**

$$S_r = 0{,}003\,2\,\mu_{1,2} + 5{,}843\,8 \qquad (35)$$

**Copper concentrates**

**Gold determination**

$$S_r = 0{,}004\,4\,\mu_{1,2} + 0{,}242\,2 \qquad (36)$$

**Silver determination**

$$S_r = 0{,}007\,5\,\mu_{1,2} + 0{,}968\,8 \qquad (37)$$

Permissible difference

$$P = 2{,}8\sqrt{S_L^2 + \frac{S_r^2}{2}} \qquad (38)$$

Range

$$E = \left|\mu_1 + \mu_2\right| \qquad (39)$$

where

$\mu_1$ is the final result, in grams of gold or silver per tonne, reported by laboratory 1;

$\mu_2$ is the final result, in grams of gold or silver per tonne, reported by laboratory 2.

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

## 9.4 Check of trueness

### 9.4.1 General

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 Clause 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:

$$\left|\mu_c - A_c\right| \le C \qquad (40)$$

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

$$\left|\mu_c - A_c\right| > C \qquad (41)$$

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

In Formulae (40) and (41), the symbols have the following meanings:

$\mu_c$ is the final result, in grams of gold or silver per tonne, of the certified reference material;

$A_c$ is the certified value, in grams of gold or silver per tonne, of the certified reference material;

$C$ is a quantity, in grams of gold or silver per tonne, depending on the type of the certified reference material used, as defined in 9.4.2.

### 9.4.2 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.

#### 9.4.2.1 Reference material certified/characterized by an interlaboratory test programme

The quantity $C$ (see 9.4.1), in grams of gold or silver per tonne, is given by Formula (24):

$$C = 2\sqrt{S_L^2 + \frac{S_r^2}{n} + S^2\{A_c\}} \tag{42}$$

where

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

$n$ is the number of replicate determinations.

#### 9.4.2.2 Reference material certified/characterized by one laboratory

The quantity $C$ (see 9.4.1), in grams of gold or silver per tonne, is given by Formula (43):

$$C = 2\sqrt{2S_L^2 + \frac{S_r^2}{n}} \tag{43}$$

NOTE 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 include the following information:

a) identification of the sample;

b) reference to this International Standard, i.e. ISO 10378;

c) mass fraction of gold of the sample, expressed in grams per tonne;

d) mass fraction of silver of the sample, expressed in grams per tonne;

e) date on which the test was carried out;

f) any occurrences 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 General

This Annex specifies a method for the preparation and determination of the mass of a predried test portion in the analysis of copper, lead, and zinc sulfide concentrates. The method is applicable to copper, lead, and zinc sulfide concentrates not susceptible to oxidation and having 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 hygroscopic moisture is required.

## A.3 Reagents

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

**WARNING — Care needs to be taken whenever disposing of exhausted magnesium perchlorate and all other laboratory chemicals. Environmental regulations often apply. Users should seek specialist's advice to determine an appropriate, effective, health-conscious, safety-conscious, and environmentally sound means of disposal.**

## A.4 Apparatus

Ordinary laboratory equipment, and the following.

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

### A.5.2 Test portion

Tare the dried weighing 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 dry mass of test portion

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 cooling 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 ($m_6$), after slightly lifting the cover and quickly replacing it. Transfer the test portion into the appropriate analytical apparatus and immediately reweigh the empty weighing vessel and its cover. Record the mass ($m_7$) to the nearest 0,1 mg.

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 $(m_6')$. The mass of the test portion can be considered to be constant if the difference between $m_6$ and $m_6'$ 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 dry mass of the test portion

The dry mass of the test portion ($m_8$), in grams, is given by Formula (A.1):

$$m_8 = m_6 - m_7 \tag{A.1}$$

where

$m_6$ is the mass, in grams, of the dried test portion plus the weighing vessel and its cover;

$m_7$ 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 mass fraction of element in the laboratory sample on a dry basis. No correction for hygroscopic moisture is required.

# Annex B

(normative)

# Trial fusion

## B.1 General

The mass of oxidizing agent, potassium nitrate or sodium nitrate (4.4) in the charge depends on the reducing power of the test sample.

A trial fusion is carried out to ensure that the test fusion yields a lead button of mass between 30 g and 45 g.

## B.2 Procedure

Mix a test portion with the appropriate masses of flux components. Typical masses of flux components for copper, lead, and zinc concentrates are shown in Tables 1 to 3, respectively.

Carry out the fusion as specified in 7.5.

Weigh the lead button obtained from the fusion. If the button weighs less than 30 g or more than 45 g, an adjustment of the oxidizing/reducing properties of the fusion mixture may be made using the following approximations:

a) the addition of 1 g of potassium nitrate will decrease the button mass by 4 g;

b) variations in the mass of the test portion will affect the button size according to the following approximation: 1 g of sulfur in the test portion will yield approximately 19 g of lead;

c) for roasted samples or other samples not giving at least 30 g of lead button, flour (4.5) may be added to increase the reducing properties of the charge; the flour shall be thoroughly mixed with the other components in the charge (for information, 1 g of flour gives approximately 10 g to 12 g of lead).

# Annex C
(normative)

# Blank determination

## C.1 General

A blank determination is carried out to determine the mass fraction of gold and silver of the assay reagents, principally litharge. It is recommended that the blank determination be performed in duplicate.

## C.2 Procedure

Thoroughly mix the flux components with sufficient flour (4.5). Typical masses of flux components for copper, lead, and zinc concentrates are shown in Tables 1 to 3, respectively, and potassium nitrate (4.4) should be omitted from the components. The amount of flour (4.5) is usually 3 g to 4 g, as a reducing agent to produce a lead button of 30 g to 45 g.

Continue the blank determination in accordance with 7.5 to 7.7.

Combine the primary and secondary blank beads and determine the gold and silver concentration of the blank solutions in accordance with 7.9.

# Annex D
(normative)

# Inquartation

## D.1 General

To ensure complete parting of the bead, the ratio of silver to gold has to exceed 2,5 to 1. Beads in which this ratio is not reached, i.e. those in which the mass fraction of gold exceeds 30 % are inquarted. However, in cases where the silver is determined by AAS or ICP, the silver cannot be determined in the inquarted bead, and so separate determinations for gold and silver will be necessary. The gold should be determined by inquartation in accordance with this annex, and the silver by the dissolution method specified in 7.9 without the parting operation.

If the silver is determined by the gravimetric method instead of the procedure specified in 7.10, weigh the primary bead before the inquartation. Inquart the bead in accordance with this annex, carry out the parting by the procedure specified in 7.8, and determine the impurities in the parting solution and washing by the procedure specified in Annex G.

NOTE 1 If the approximate silver to gold ratio is known to be less than 2,5 to 1, the appropriate mass of silver to give a ratio of 4 to 1 can be added prior to the first fusion.

NOTE 2 If the mass of the gold is less than 50 µg, the bead can be dissolved without parting and the gold and silver concentration can be determined as specified in 7.9. In such cases, inquartation is not necessary.

Silver should be determined by the method in 7.9 without parting, provided that the product of mass of the test portion by mass fraction of the silver, i.e. mass in the test portion, is smaller than 7 500 µg. The test portion of 20 g, therefore, is too much to determine the silver, where the mass fraction of the element exceeds 325 g/t.

## D.2 Procedure

Weigh the bead prior to any attempt at parting ($m_0$).

Add a mass of silver (4.10) sufficient to obtain a silver to gold ratio of 4 to 1.

Wrap the bead and the silver together in 0,5 g of lead foil (4.9), cupel in accordance with 7.6 to obtain a silver-rich bead and determine the mass fraction of gold as specified in 7.8.

# Annex E
(normative)

# Determination of vaporization loss of silver during the cupellation process

## E.1 General

To prevent loss of silver during the cupellation process, it is very important that furnace conditions be as specified in 7.6. It is recommended that the loss of silver during the cupellation process be determined, to decide upon the furnace conditions.

If complete recovery is not obtained, the mass fraction of silver of the test portion shall be corrected.

## E.2 Procedure

Weigh the same mass of silver (4.10) as the mass fraction of silver in the test portion. Wrap it in 40 g of lead foil (4.9) and cupel in accordance with 7.6 to obtain a silver bead. Retreat the cupel in accordance with 7.7 and combine the primary and secondary beads in the porcelain crucible.

Add 10 ml of dilute nitric acid (4.8) to the beads in the porcelain crucible and heat gently on a hotplate (5.13) for 20 min, or until the reaction ceases.

Determine silver concentration of the solutions in accordance with 7.10.

## E.3 Calculation of loss of silver during the cupellation process

Loss of silver during the cupellation process ($L_{\mathrm{Ag}}$), expressed in percent, is given by Formula (E.1):

$$L_{\mathrm{Ag}} = \frac{m - m_1}{m} \times 100 \qquad \text{(E.1)}$$

where

$m_1$ is the mass, in micrograms, of silver in the solutions;

$m$ is the mass, in micrograms, of the silver metal weighed.

## E.4 Correction of mass fraction of silver of the test portion

If sufficient recovery of silver during the cupellation process is not obtained, the mass fraction of silver of the test portion $(w'_{\mathrm{Ag}})$, expressed in grams per tonne, should be corrected by Formula (E.2):

$$w'_{\mathrm{Ag}} = \frac{w_{\mathrm{Ag}}}{100 - L_{\mathrm{Ag}}} \times 100 \qquad \text{(E.2)}$$

where

$w'_{\mathrm{Ag}}$ is the mass fraction of silver, in grams per tonne, of test portion calculated by Formula (3);

$L_{\mathrm{Ag}}$ is the loss of silver, in percent, calculated by Formula (E.1).

# Annex F

(normative)

# Sulfuric acid — Parting

## F.1 General

If there is danger of the gold sponge crumbling during the parting operation, it is recommended that the operation be carried out with sulfuric acid.

## F.2 Reagent

**F.2.1 Sulfuric acid**, concentrated ($\rho_{20}$ 1,84 g/ml), chloride content <0,5 µg/ml.

**F.2.2 Sulfuric acid**, diluted 1 + 5.

Slowly add 200 ml of concentrated sulfuric acid (F.2.1) to 1 000 ml of water, while stirring.

## F.3 Apparatus

**F.3.1 Parting flask**, of capacity 60 ml.

## F.4 Procedure

Transfer the bead prepared in 7.6 to a parting flask and add 5 ml to 20 ml of sulfuric acid (F.2.1). Dissolve the silver by gently heating for 5 min to 10 min.

NOTE 1 It is essential that chloride be absent during parting; otherwise, some of the gold may dissolve.

When the bead is treated with hot sulfuric acid, silver will start to dissolve, provided that the ratio of silver to gold in the bead exceeds 2,5 to 1. The rate of dissolution increases with increasing mass fraction of silver of the bead. Rapid attack of the bead should be avoided by further dilution and slow heating to prevent disintegration of the gold. Should the ratio of silver to gold be less than 2,5 to 1 as shown by failure to part in hot sulfuric acid, the bead should be inquarted (see Annex D).

After cooling, carefully pour the solution into a 200 ml beaker by decantation to avoid losses.

Wash the flask and gold with several 10 ml to 20 ml volumes of dilute sulfuric acid (F.2.2), followed by several 10 ml to 20 ml volumes of hot water, and carefully pour the solutions into the 200 ml beaker by decantation to avoid losses. Collect all the washings in the same 200 ml beaker.

Reserve the solution for the determination of silver as specified in 7.10.

For the determination of silver in 7.10, prepare the calibration solutions to contain the same concentrations of sulfuric acid as the test solutions.

NOTE 2 The possibility of gold particles occurring in the collected parting and washing solutions can be determined by evaporating the solutions slowly down to 2 ml to 3 ml, then continuing with the determination as specified in 7.9.

Fill the parting flask with water and cover with a 30 ml porcelain crucible. Turn the flask upside down in order to sink the gold into the crucible. Remove the flask and discard the water in the crucible by careful decantation.

Dry the gold sponge in the porcelain crucible on the hotplate.

Place the crucible in the muffle furnace (5.2) to anneal the gold at dull red heat for approximately 5 min.

Cool and weigh the gold, in micrograms, to the nearest 1 µg ($m_1$).

If the mass of the gold is less than 50 µg, it is recommended that the gold be dissolved and determined by the procedure specified in 7.9.

If the mass of the gold is less than 50 µg, repeat the fusion and cupellation, then dissolve the prepared bead and determine the gold and silver concentrations as specified in 7.9 without parting. This procedure, however, cannot be applied if the product of mass of test portion by mass fraction of silver, i.e. mass in test portion, is larger than 7 500 µg.

If the sensitivity of the microbalance is 0,1 µg, the applicable range of the gravimetric method can be extended to 5 µg of gold. In such cases, weigh the gold prill, in micrograms, to the nearest 0,1 µg ($m_1$).

Reserve the gold prill to determine silver in the prill by combining several of the weighed prills of the same laboratory sample, dissolving these and determining the silver concentration as specified in 7.9.

Platinum and palladium are removed from the prill during parting with nitric acid. If the determination of these elements remaining in the prill is considered necessary, determine these by the procedure specified in 7.9 followed by the addition of platinum and palladium to the standard solutions in relevant proportions. If a sufficient detection limit for AAS or ICP cannot be obtained on a single prill basis, a large number of prills of the same laboratory sample should be combined.

# Annex G
(normative)

# Determination of impurities in parting solutions and washings

## G.1 General

If the mass fraction of silver in the sample is high, the gravimetric method is recommended for the accurate determination of silver. For this method, it is necessary to determine impurities in the parting solution and washing in accordance with this Annex.

## G.2 Reagent

**G.2.1 Hydrochloric acid**, diluted 1 + 1.

Slowly add 500 ml of concentrated hydrochloric acid (4.11) to 500 ml of water, while stirring.

**G.2.2 Bismuth**, minimum purity 99,99 %.

**G.2.3 Lead**, minimum purity 99,99 %.

**G.2.4 Palladium**, minimum purity 99,99 %.

**G.2.5 Platinum**, minimum purity 99,99 %.

**G.2.6 Magnesium oxide**, minimum purity 99 %.

**G.2.7 Calcium carbonate**, minimum purity 99,99 %.

**G.2.8 Standard solutions**.

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

**G.2.8.1 Bismuth**, standard stock solution A (500 µg of Bi/ml).

Weigh 0,500 0 g of bismuth metal (G.2.2) to the nearest 0,1 mg. Transfer to a 100 ml beaker, add 20 ml of dilute nitric acid (4.8) and warm to dissolve. Cool and 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.

**G.2.8.2 Bismuth**, standard solution B (20 µg of Bi/ml).

Pipette 10,00 ml of bismuth standard stock solution A (G.2.8.1) into a 250 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.

**G.2.8.3 Lead**, standard stock solution A (500 µg of Pb/ml).

Weigh 0,500 0 g of lead metal (G.2.3) to the nearest 0,1 mg. Transfer to a 100 ml beaker, add 20 ml of dilute nitric acid (4.8) and warm to dissolve. Cool and 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.

**G.2.8.4 Lead**, standard solution B (10 µg of Pb/ml).

Pipette 10,00 ml of lead standard stock solution A (G.2.8.3) into a 500 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.

**G.2.8.5 Palladium**, standard stock solution A (200 µg of Pd/ml).

Weigh 0,100 0 g of palladium metal (G.2.4) to the nearest 0,1 mg. Transfer to a 100 ml beaker, add 10 ml of aqua regia (4.13) and warm to dissolve. Cool and transfer to a 500 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.

**G.2.8.6 Palladium**, standard solution B (10 µg of Pd/ml).

Pipette 10,00 ml of palladium standard stock solution A (G.2.8.5) into a 200 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.

**G.2.8.7 Platinum**, standard stock solution A (1 000 µg of Pt/ml).

Weigh 0,100 0 g of platinum metal (G.2.5) to the nearest 0,1 mg. Transfer to a 100 ml beaker, add 10 ml of aqua regia (4.13) and warm to dissolve. Cool and transfer to a 100 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.

**G.2.8.8 Platinum**, standard solution B (50 µg of Pt/ml).

Pipette 10,00 ml of platinum standard stock solution A (G.2.8.7) to a 200 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.

**G.2.8.9 Magnesium**, standard stock solution A (500 µg of Mg/ml).

Weigh 0,829 g of magnesium oxide (G.2.6) to the nearest 0,1 mg. Transfer to a 100 ml beaker, add 20 ml of dilute hydrochloric acid (G.2.1), and warm to dissolve. Cool and 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.

**G.2.8.10 Magnesium**, standard solution B (5 µg of Mg/ml).

Pipette 10,00 ml of magnesium standard stock solution A (G.2.8.9) into 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.

**G.2.8.11 Calcium**, standard stock solution A (500 µg of Ca/ml).

Weigh 1,249 0 g of calcium carbonate (G.2.7) to the nearest 0,1 mg. Transfer to a 100 ml beaker, add 20 ml of dilute hydrochloric acid (G.2.1), and warm to dissolve. Cool and 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.

**G.2.8.12 Calcium**, standard solution B (20 µg of Ca/ml).

Pipette 10,00 ml of calcium standard stock solution A (G.2.8.11) into a 250 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.

### G.2.9 Bismuth/lead/palladium/platinum/magnesium/calcium calibration solutions

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

Pipette 0,0 ml, 1,00 ml, 2,00 ml, 3,00 ml, and 5,00 ml of bismuth standard solution (G.2.8.2), lead standard solution (G.2.8.4), palladium standard solution (G.2.8.6), platinum standard solution (G.2.8.8), magnesium standard solution (G.2.8.10), and calcium standard solution (G.2.8.12) into a series of 50 ml one-mark volumetric flasks.

Add 5 ml of aqua regia (4.13) to each flask, fill up nearly to the mark with water, mix and cool to room temperature; then fill up exactly to the mark and mix again.

These solutions contain 0,0 µg of Bi, Ca/ml, 0,40 µg of Bi, Ca /ml, 0,80 µg of Bi, Ca /ml, 1,20 µg of Bi, Ca / ml and 2,00 µg of Bi, Ca /ml; 0,0 µg of Pb, Pd/ml, 0,20 µg of Pb, Pd /ml, 0,40 µg of Pb, Pd /ml, 0,60 µg of Pb, Pd /ml and 1,00 µg of Pb,Pd /ml; 0,0 µg of Pt/ml, 1,00 µg of Pt/ml, 2,00 µg of Pt/ml, 3,00 µg of Pt/ml and 5,00 µg of Pt/ml; and 0,0 µg of Mg/ml, 0,10 µg of Mg/ml, 0,20 µg of Mg/ml, 0,30 µg of Mg/ml, and 0,50 µg of Mg/ml, respectively, and shall be freshly prepared.

## G.3 Procedure

Take the parting solutions and washings that were reserved in 7.8. Heat to evaporate to dryness. Add 5 ml of aqua regia (4.13) and warm to dissolve. Cool and transfer to a 50 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.

Aspirate the test solutions and bismuth/lead/palladium/platinum/magnesium/calcium calibration solutions (G.2.9) into the atomic absorption spectrometer (5.10) and measure the absorbance. As a guide, the atomic absorption settings shown in Table G.1 are recommended. However, the instrument should be optimized to be free from any interference and to give maximum sensitivity and as near as practical to a linear relationship between absorbance and concentration.

**Table G.1 — Recommended atomic absorption settings**

| Parameter | Bismuth | Lead | Palladium | Platinum | Magnesium | Calcium |
|---|---|---|---|---|---|---|
| Flame | air/acetylene(oxidizing) | | | | | $N_2O$/acetylene |
| Wavelength | 223,1 nm | 283,3 nm | 244,8 nm | 265,9 nm | 285,2 nm | 422,7 nm |
| Lamp current | 10 mA | 5 mA | 5 mA | 10 mA | 4 mA | 10 mA |
| Background corrector | on | on | on | on | on | on |
| Aspiration rate | optimize for maximum signal | | | | | |
| Integration time | 3 s | | | | | |
| Number of integrations | 5 | | | | | |
| Absorbance of 1 µg/ml calibration solution | 0,02 | 0,04 | 0,05 | 0,003 | 0,15 (0,1 µg of Mg/ml) | 0,25 |

NOTE 1 The measurements of elements that are impossible to be contained in the parting solution and washings can be skipped.

NOTE 2 If silver chloride precipitates, the top clear layer solution can be used as the test solution.

In order to clean out the nebulizer system, it is recommended to aspirate the cleaning solution, which is, for instance, prepared by carefully adding 500 ml of hydrochloric acid (4.11) and 100 ml of concentrated nitric acid (4.7) to 400 ml of water, between measurements.

Plot a calibration graph absorbance versus concentration and determine the bismuth, lead, palladium, platinum, magnesium, and/or calcium concentrations, in micrograms per millilitre, in the test solutions, followed by calculation of the mass ($m_a$), in micrograms, of the metals using Formula (G.1):

$$m_a = \rho \times 50 \qquad \text{(G.1)}$$

where $\rho$ is the mass concentration of each metal.

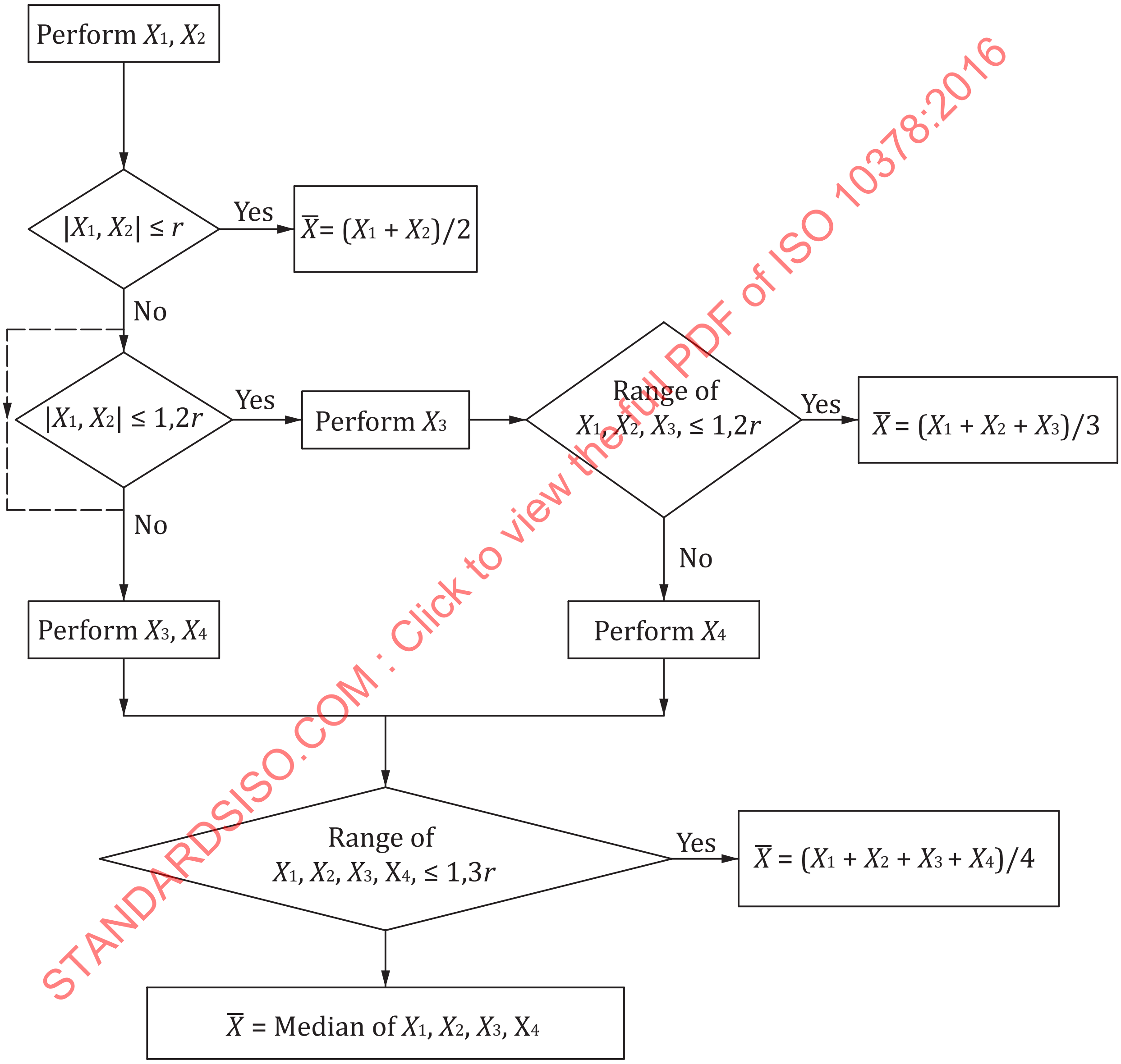
Sum up the mass of all elements determined to calculate the amount of impurities in the parting solution and washings ($m_{imp}$).

Alternatively, an ICP atomic emission spectrometer (5.11) can be used for the determination of bismuth, lead, palladium, platinum, magnesium, and calcium at the appropriate wavelength. Typical wavelengths are 223,06 nm for bismuth, 220,35 nm for lead, 340,46 nm for palladium, 214,42 nm for platinum, 279,55 nm for magnesium, and 393,37 nm for calcium. However, the instrument should be optimized to be free from any interference and to give maximum sensitivity and as near as practical to a linear relationship between absorbance and concentration.

During all AAS or ICP determinations, the test solutions and calibration solutions should have the same temperature as well as the same acid(s) concentration.

# Annex H
(normative)

# Flowsheet of the procedure for the acceptance of analytical values for test samples (see 9.2)



# Annex I
(informative)

## Flowsheet of the method

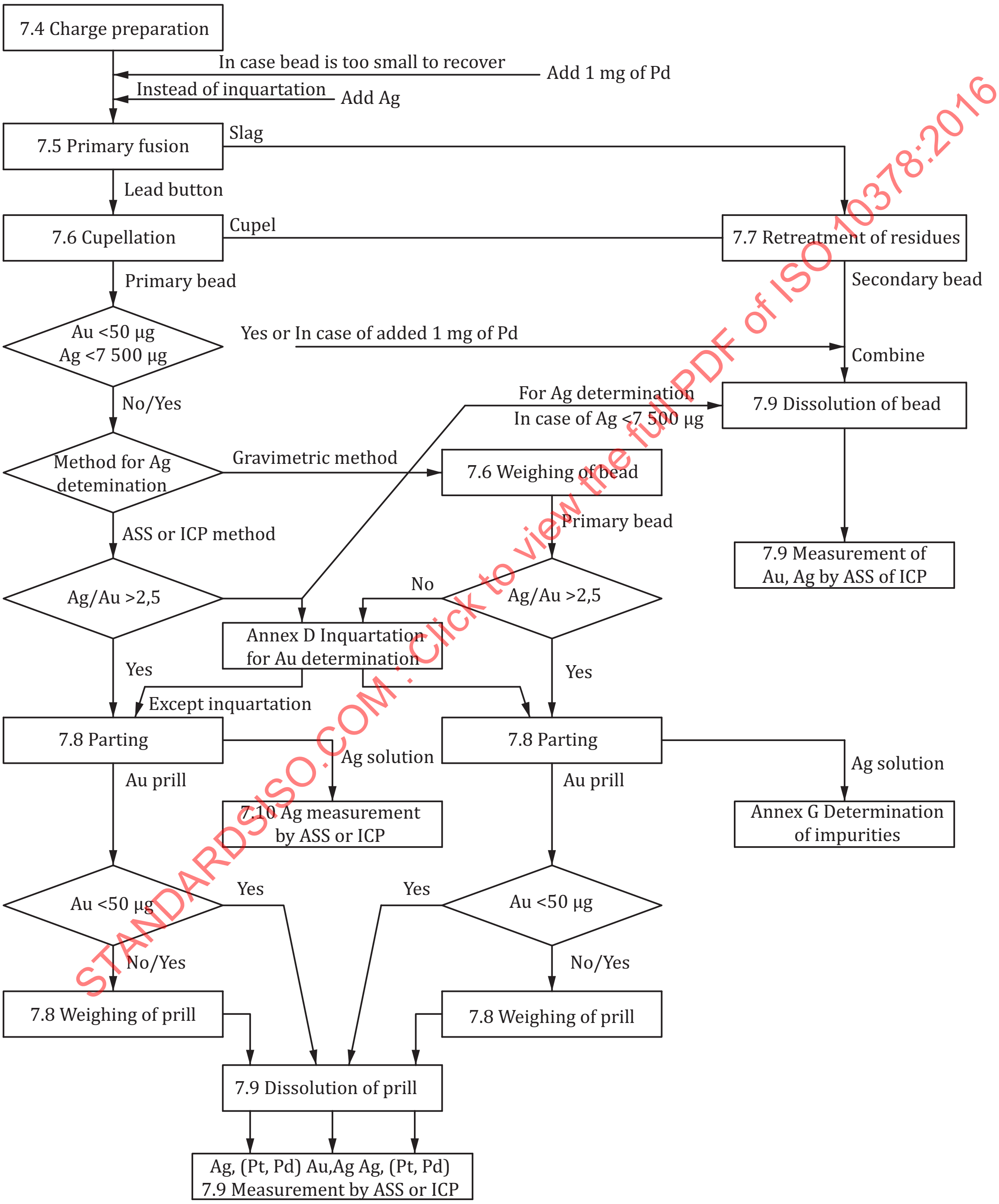


**Figure I.1 — Flowsheet of the method**

# Annex J
(informative)

# Roasting method

## J.1 General

If arsenic is present in the sample at a mass fraction above 2 %, this may cause interference with the cupellation procedure. The following roasting procedure will remove this element by volatilizing it as sulfide.

## J.2 Procedure

Weigh the test portion (6.2) into a roasting dish that has been coated with chalk or litharge to prevent sticking. Spread the test portion evenly on the coating.

Place the dish in the muffle furnace (5.2) maintained at 450 °C for 2 h.

Gradually increase the temperature of the muffle furnace to 600 °C and heat for another 2 h. Stir the test portion every 30 min during roasting.

Remove the dish from the muffle furnace and cool. Transfer the test portion and thoroughly mix with the flux components, using part of the litharge as a coating.

Continue with the primary fusion (7.5), but in this case determine the amount of flour required in the charge.

# Annex K
(informative)

# Guide to the preparation of dilutions for the determination of silver in parting solutions and residues

See Tables K.1 and K.2.

**Table K.1 — Gold and silver in test solutions in 7.9**

| Mass in test potion<br>µg | | Original volume | Aliquot to take | Final volume | Total dilution factor |
|---|---|---|---|---|---|
| **Gold** | **Silver** | ml | ml | ml | 50 |
| <50 | <250 | 50 | 50 | 50 | 50 |
| — | 250 to 500 | 50 | 20 | 50 | 125 |
| — | 500 to 1 200 | 50 | 10 | 50 | 250 |
| — | 1 200 to 2 400 | 50 | 10 | 100 | 500 |
| — | 2 400 to 4 800 | 50 | 10 | 200 | 1 000 |
| — | 4 800 to 7 500 | 50 | 10 | 500 | 2 500 |

**Table K.2 — Silver in test solutions in 7.10**

| Mass of silver in test portion<br>µg | Original volume<br>ml | Aliquot to take<br>ml | Final volume<br>ml | Total dilution factor |
|---|---|---|---|---|
| <500 | 100 | 100 | 100 | 100 |
| 500 to 1 000 | 100 | 20 | 50 | 250 |
| 1 000 to 2 000 | 100 | 20 | 100 | 500 |
| 2 000 to 4 000 | 100 | 10 | 100 | 1 000 |
| 4 000 to 8 000 | 100 | 10 | 200 | 2 000 |
| 8 000 to 20 000 | 100 | 10 | 500 | 5 000 |
| 20 000 to 40 000 | 100 | 10 | 1 000 | 10 000 |

NOTE The mass in the test portion is the product of the mass of test portion and the concentration of gold and silver.

# Annex L
(informative)

# Derivation of precision equations

## L.1 General

This international Standard was tested in an interlaboratory test programme involving 5 countries and 16 laboratories. The following samples were analysed.

a) Five samples of zinc concentrate covering the range 0,1 g/t to 2,3 g/t of gold and 42 g/t to 780 g/t of silver.

b) Six samples of lead concentrate covering the range 0,1 g/t to 6,7 g/t of gold and 390 g/t to 3 200 g/t of silver.

c) Five samples of copper concentrate covering the range 0,3 g/t to 200 g/t of gold and 60 g/t to 680 g/t of silver.

The test programme was designed to determine the repeatability and within-laboratory and between-laboratories reproducibilities in general, using the principles of ISO 5725-2.

## L.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 analysed twice independently.

## L.3 Test samples

This test programme used five samples of zinc concentrate, six samples of lead concentrate, and five samples of copper concentrate. The composition of these samples is given in Tables L.1, L.2, and L.3.

## L.4 Statistical evaluation

The procedure for statistical evaluation is illustrated schematically in Figure L.1. The results of the statistical evaluation are summarized in Tables L.4. to L.9.

The estimated precisions ($S_r$, $S_L$, $r$, and $P$) are plotted against their corresponding sample means on a graph as shown in Figures L.2 to L.7, and the regression equations of these precisions against sample means were computed and are presented in Tables L.4 to L.9.

### Table L.1 — Composition of zinc concentrate samples

| Element | | Sample numbers | | | | |
|---|---|---|---|---|---|---|
| | | 2001-Zn-1 | 2001-Zn-2 | 2001-Zn-3 | 2001-Zn-4 | 2001-Zn-5 |
| Zn | % (*m*/*m*) | 49 | 50 | 54 | 36 | 49 |
| Pb | % (*m*/*m*) | 3 | 0,9 | 1 | 15 | 3 |
| Cu | % (*m*/*m*) | 0,3 | 0,6 | 1 | 0,6 | 0,3 |
| Au | g/t | <0,1 | <0,1 | 2 | 0,1 | 0,4 |
| Ag | g/t | 160 | 79 | 43 | 790 | 520 |
| S | % (*m*/*m*) | 30 | 33 | 32 | 28 | 31 |
| As | % (*m*/*m*) | 0,01 | 0,03 | 0,03 | 0,31 | 0,06 |
| Sb | % (*m*/*m*) | 0,01 | <0,01 | <0,01 | 0,23 | 0,02 |
| Sn | % (*m*/*m*) | <0,01 | <0,01 | <0,01 | 0,35 | <0,01 |
| Bi | % (*m*/*m*) | <0,01 | <0,01 | <0,01 | 0,10 | <0,01 |
| Fe | % (*m*/*m*) | 8 | 10 | 6 | 10 | 10 |
| $SiO_2$ | % (*m*/*m*) | 3 | 1 | 1 | 2 | 2 |
| $Al_2O_3$ | % (*m*/*m*) | 0,6 | 0,2 | 0,2 | 0,5 | 0,09 |
| CaO | % (*m*/*m*) | 0,9 | 0,1 | 0,1 | 0,1 | 0,2 |
| MgO | % (*m*/*m*) | 0,5 | 0,2 | 0,03 | 0,05 | 0,5 |
| Cd | % (*m*/*m*) | 0,2 | 0,1 | 0,3 | 0,2 | 0,3 |
| Ni | % (*m*/*m*) | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 |
| Co | % (*m*/*m*) | <0,01 | 0,02 | <0,01 | <0,01 | <0,01 |

**Table L.2 — Composition of lead concentrate samples**

| Element | | Sample numbers | | | | | |
|---|---|---|---|---|---|---|---|
| | | **2001-Pb-1** | **2001-Pb-2** | **2001-Pb-3** | **2001-Pb-4** | **2001-Pb-5** | **2001-Pb-6** |
| Pb | % (*m*/*m*) | 65 | 33 | 65 | 57 | 50 | 72 |
| Zn | % (*m*/*m*) | 6 | 5 | 10 | 12 | 7 | 4 |
| Cu | % (*m*/*m*) | 1 | 2 | 0,8 | 0,07 | 0,2 | 0,3 |
| Au | g/t | 70 | 3 | 4 | <0,1 | <0,1 | 0,5 |
| Ag | g/t | 2200 | 660 | 1300 | 390 | 1100 | 3200 |
| S | % (*m*/*m*) | 17 | 30 | 17 | 19 | 23 | 14 |
| As | % (*m*/*m*) | 0,3 | 0,5 | 0,1 | 0,03 | 0,03 | 0,03 |
| Sb | % (*m*/*m*) | 0,2 | 0,2 | 0,3 | 0,1 | 0,09 | 0,2 |
| Sn | % (*m*/*m*) | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 |
| Bi | % (*m*/*m*) | 0,4 | 0,02 | 0,02 | <0,01 | <0,01 | <0,01 |
| Fe | % (*m*/*m*) | 4 | 20 | 3 | 5 | 11 | 3 |
| $SiO_2$ | % (*m*/*m*) | 2 | 0,5 | 0,7 | 3 | 2 | 3 |
| $Al_2O_3$ | % (*m*/*m*) | 0,3 | 0,07 | 0,3 | 0,1 | 0,5 | 0,1 |
| CaO | % (*m*/*m*) | 0,9 | 0,7 | 0,04 | 0,06 | 0,5 | 0,3 |
| MgO | % (*m*/*m*) | 0,3 | 0,2 | 0,06 | 0,01 | 0,3 | 0,7 |
| Cd | % (*m*/*m*) | 0,03 | 0,01 | 0,03 | 0,2 | 0,03 | 0,02 |
| Ni | % (*m*/*m*) | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 | <0,01 |
| Co | % (*m*/*m*) | <0,01 | <0,01 | <0,01 | 0,02 | 0,01 | <0,01 |

**Table L.3 — Composition of copper concentrate samples**

| Element | | Sample numbers | | | | |
|---|---|---|---|---|---|---|
| | | 2001-Cu-1 | 2001-Cu-2 | 2001-Cu-3 | 2001-Cu-4 | 2001-Cu-5 |
| Cu | % ($m/m$) | 33 | 24 | 37 | 26 | 37 |
| Zn | % ($m/m$) | 0,2 | 0,06 | 0,1 | 4 | 0,08 |
| Pb | % ($m/m$) | 0,04 | 0,02 | 0,03 | 4 | 0,02 |
| Au | g/t | 54 | 53 | 0,9 | 0,4 | 200 |
| Ag | g/t | 69 | 62 | 120 | 670 | 590 |
| S | % ($m/m$) | 27 | 27 | 27 | 32 | 21 |
| As | % ($m/m$) | <0,02 | 0,04 | 0,08 | <0,02 | 0,1 |
| Sb | % ($m/m$) | <0,02 | <0,02 | <0,02 | 0,1 | <0,02 |
| Sn | % ($m/m$) | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 |
| Bi | % ($m/m$) | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 |
| Fe | % ($m/m$) | 22 | 23 | 20 | 28 | 16 |
| $SiO_2$ | % ($m/m$) | 10 | 16 | 9 | 2 | 11 |
| $Al_2O_3$ | % ($m/m$) | 2 | 4 | 2 | 0,4 | 1 |
| CaO | % ($m/m$) | 0,6 | 1 | 0,7 | 0,09 | 9 |
| MgO | % ($m/m$) | 0,5 | 0,6 | 0,1 | 0,09 | 1 |
| Cd | % ($m/m$) | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 |
| Ni | % ($m/m$) | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 |
| Co | % ($m/m$) | <0,02 | <0,02 | <0,02 | 0,02 | 0,02 |

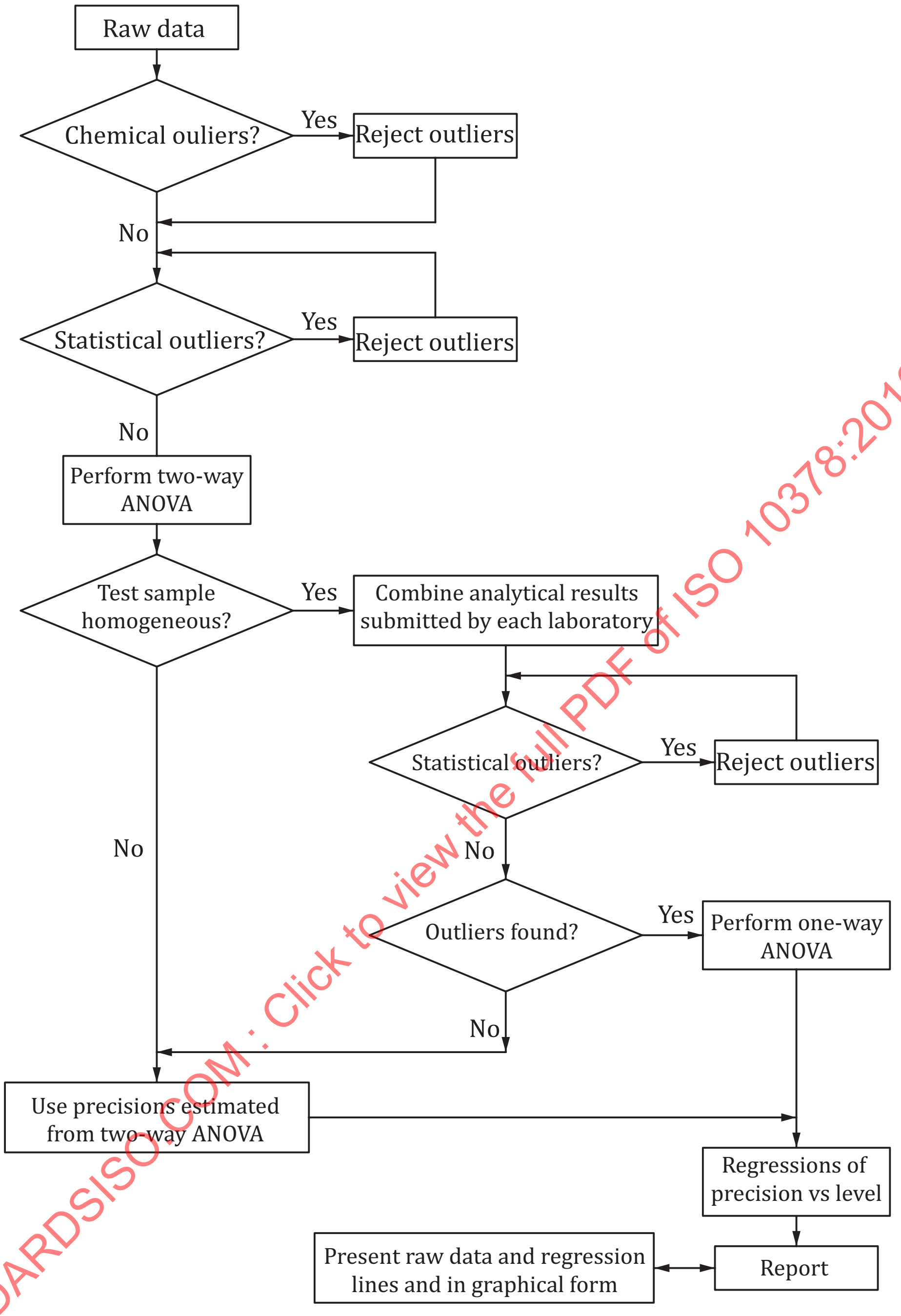


**Figure L.1 — Flowsheet of procedure for statistical evaluation of analytical data resulting from international tests**

### Table L.4 — Summary of precisions for zinc concentrate samples — Gold

| **Sample number**<br>(see Table L.1) | $K_0$ | $k$ | $n_0$ | $n$ | $\overline{\overline{X}}$ | $r$ | $P$ | $S_r$ | $S_L$ | $S_L/S_r$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **2001-Zn-1** | 8 | 8 | 31 | 31 | 0,044 | 0,082 | 0,130 | 0,029 | 0,042 | 1,415 |
| **2001-Zn-2** | 8 | 8 | 31 | 31 | 0,901 | 0,226 | 0,327 | 0,081 | 0,102 | 1,262 |
| **2001-Zn-3** | 8 | 8 | 31 | 31 | 2,292 | 0,207 | 0,502 | 0,074 | 0,171 | 2,313 |
| **2001-Zn-4** | 8 | 8 | 31 | 31 | 0,107 | 0,082 | 0,131 | 0,029 | 0,042 | 1,445 |
| **2001-Zn-5** | 8 | 8 | 31 | 31 | 0,160 | 0,079 | 0,299 | 0,028 | 0,105 | 3,724 |

| **The regression formulae are** | **Correlation coefficient** |
|---|---|
| $r = 0{,}063\,0\ \overline{X} + 0{,}091\,1$ | 0,805 2 |
| $P = 0{,}147\,6\ \overline{X} + 0{,}174\,5$ | 0,908 7 |
| $S_r = 0{,}022\,5\ \overline{X} + 0{,}032\,5$ | 0,805 2 |
| $S_L = 0{,}050\,4\ \overline{X} + 0{,}057\,1$ | 0,894 7 |

$K_0$ Total number of participating laboratories.

$k$ Number of participating laboratories used for computation of precision.

$n_0$ Total number of analytical results.

$n$ Number of analytical results used for computation of precision.

$\overline{\overline{X}}$ Overall mean of the mass fraction of gold, in grams per tonne, of the sample.

$r$ Permissible within-laboratory tolerance (repeatability), in grams of gold per tonne.

$P$ Permissible between-laboratories tolerance, in grams of gold per tonne.

$S_r$ Within-laboratory standard deviation, in grams of gold per tonne.

$S_L$ Between-laboratories standard deviation, in grams of gold per tonne.

$\overline{X}$ Mean mass fraction of gold, in grams per tonne, of the sample.