INTERNATIONAL STANDARD

ISO 13547-2

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Copper, lead, zinc and nickel sulfide concentrates — Determination of arsenic —

Part 2:
Acid digestion and inductively coupled plasma atomic emission spectrometric method

Concentrés sulfurés de cuivre, de plomb et de zinc — Dosage de l'arsenic —

Partie 2: Méthode par digestion acide et plasma induit par haute fréquence

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

ISO 13547 consists of the following parts, under the general title *Copper, lead, zinc and nickel sulfide concentrates — Determination of arsenic*:

— *Part 1: Iron hydroxide concentration and inductively coupled plasma atomic emission spectrometric*

— *Part 2: Acid digestion and inductively coupled plasma atomic emission spectrometric method*

Copper, lead, zinc and nickel sulfide concentrates — Determination of arsenic —

Part 2:
Acid digestion and inductively coupled plasma atomic emission 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 an acid digestion and inductively coupled plasma atomic emission spectrometric (ICP-AES) method for the determination of the mass fraction of arsenic in copper, lead, zinc, and nickel sulfide concentrates as follows:

a) for copper sulfide concentrates, the method is applicable to the determination of mass fractions of arsenic from 0,05 % to 2,0 %;

b) for lead sulfide concentrates, the method is applicable to the determination of mass fractions of arsenic from 0,05 % to 1,0 %;

c) for zinc sulfide concentrates, the method is applicable to the determination of mass fractions of arsenic from 0,05 % to 0,6 %;

d) for nickel sulfide concentrates, the method is applicable to the determination of mass fraction of arsenic from 0,05 % to 1,0 %.

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 648, *Laboratory glassware — Single-volume pipettes*

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

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

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

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

ISO 12743:2006, *Copper, lead, zinc and nickel concentrates — Sampling procedures for determination of metal and moisture content*

3 Principle

The test portion is decomposed in nitric and sulphuric acids and arsenic is determined by comparison against matrix-matched standards using ICP-AES.

4 Reagents

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

4.1 Sodium hydroxide (NaOH), AR grade.

4.2 Arsenic trioxide (As$_2$O$_3$), AR grade.

4.3 Iron(III) chloride hexahydrate (FeCl$_3$•6H$_2$O), AR grade (<0,000 05 % Arsenic).

4.4 Copper metal (≥99,99 %).

4.5 Zinc metal (≥99,99 %).

4.6 Lead metal (≥99,99 %).

4.7 Nickel metal (≥99,99 %).

4.8 Ammonium acetate, AR grade.

4.9 Nitric acid (ρ_{20} 1,42 g/ml).

4.10 Nitric acid, dilute (1 + 1).

Slowly add 50 ml of nitric acid (4.9) to 50 ml of water while stirring.

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

4.12 Hydrochloric acid, dilute (1 + 1).

Slowly add 50 ml of hydrochloric acid (4.11) to 50 ml of water while stirring.

4.13 Sulphuric acid (ρ_{20} 1,84 g/ml).

4.14 Sulphuric acid, dilute (1 + 1).

Slowly add 50 ml of sulphuric acid (4.12) to 50 ml of water while stirring.

The addition of sulphuric acid to water generates heat and shall be performed with adequate precautions.

4.15 Sulphuric acid, dilute (1 + 50).

Slowly and with stirring, add 20 ml of sulphuric acid (4.12) to 1 000 ml of water.

4.16 Hydrofluoric acid (ρ_{20} 1,13 g/ml).

4.17 Sodium hydroxide solution (20 % w/v).

Weigh 20,0 g of sodium hydroxide (4.1) in a polytetrafluoroethylene beaker (5.5). Add 50 ml of water and allow the solid to dissolve. Dilute the solution to 100 ml and store in a labelled polyethylene container.

4.18 Saturated solution of potassium chlorate in nitric acid.

Superfluous potassium chlorate is added into the nitric acid and then the deposited solution is allowed to form the saturated solution.

4.19 Ammonium acetate (25 % w/v).

Dissolve 25,0 g of ammonium acetate (4.8) into 100 ml water.

4.20 Arsenic standard, 1 ml contains 1 mg of As.

Weigh 1 320,3 g of arsenic trioxide (4.2) into a 400 ml beaker and add 5 ml of sodium hydroxide solution (4.17). Warm slightly to dissolve. When dissolution is complete, cool and add 40 ml of nitric acid (4.9). Transfer to a 1 000 ml volumetric flask containing 60 ml of nitric acid (4.9). Fill up nearly to the mark with water, mix, and equilibrate at room temperature, then fill up exactly to the mark and mix again. Store in a labelled container.

Alternatively, purchase a suitable high quality prepared standard.

Before use, compare this International Standard against a traceable National Standard to ensure suitability for use.

4.21 Arsenic standard, 1 ml contains 0,2 mg of As.

Pipette 40 ml of arsenic standard (4.20) into a 200 ml volumetric flask containing 2 ml hydrochloric acid (4.11). Fill up nearly to the mark with water, mix, and equilibrate at room temperature, then fill up exactly to the mark and mix again. Store in a labelled glass container.

4.22 Copper matrix/interference standard (25,0 mg/ml).

Dissolve 2,5 g of copper metal (4.4) with 50 ml of warm dilute nitric acid (4.10). Evaporate to approximately 25 ml in order to remove nitrogen oxides. Transfer to a 100 ml volumetric flask, add 5 ml concentrated hydrochloric acid, then fill up with water nearly to the mark. Mix and cool to room temperature, then fill up exactly to the mark and mix again.

4.23 Zinc matrix/interference standard (32,5 mg/ml).

Dissolve 3,25 g of zinc metal (4.5) with 50 ml of warm dilute hydrochloric acid (1+1). 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.

4.24 Iron matrix/interference standard (10 mg/ml).

Dissolve 48,4 g iron (III) chloride hexahydrate (4.3) in 200 ml of water. Add 10 ml of hydrochloric acid (4.11) and make up to 1 000 ml with water and mix.

4.25 Lead matrix/interference standard (37,5 mg/ml).

Dissolve 3,75 g of lead metal (4.6) by adding 40 ml of water and 20 ml of nitric acid (4.9) and heat to dissolve. 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.

4.26   Nickel matrix/interference standard (10 mg/ml).

Dissolve 1,0 g of nickel metal (4.7) in 50 ml of dilute nitric acid (4.10) and heat until all nitrogen oxides are expelled. The volume will be about 25 ml. Transfer to a 100 ml volumetric flask. Add 25 ml of hydrochloric acid (4.11) and fill up with water nearly to the mark, mix, and cool to room temperature, then fill up exactly to the mark and mix again.

5   Apparatus

All laboratory glassware and equipment shall be shown to be free of arsenic contamination.

5.1   Balance, sensitive to ±0,1 mg.

5.2   Normal laboratory glassware, complying with ISO 648 and ISO 1042 and used in accordance with ISO 4787.

5.3   Inductively coupled plasma atomic emission spectrometer (ICP-AES).

The emission wavelength should be set to 193,696 nm or 197,197 nm.

5.4   Insolubles filter paper, Whatman®[1] No. 40 or equivalent.

5.5   Polytetrafluoroethylene beaker, 200 ml capacity.

6   Sampling and sample preparation

6.1   Laboratory sample

Laboratory samples shall be taken and prepared in accordance with the procedures described in ISO 12743.

As arsenic can evaporate from samples at elevated temperatures, consideration should be given to preparing a separate chemical analysis sample as described in ISO 12743:2006, 16.2.

6.2   Test sample

Prepare an air-equilibrated test sample and a hygroscopic moisture test sample in accordance with ISO 9599.

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

6.3   Test portion

Taking multiple increments, extract approximately 0,5 g from the test sample and weigh to the nearest 0,1 mg. At the same time, as the test portions are being weighed for analysis, 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 pre-dried test portions directly from the laboratory sample.

Obtain an approximate concentration for the copper, lead, zinc, and iron in the sample as required in step 7.7.

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1)   This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO.

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   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 the same quantities of all reagents, but omitting the sample. The purpose of the blank test is to check for contamination of the apparatus used in the test and the purity of the reagents.

7.3 Dissolution of the test portion

Quantitatively, transfer the test portion into a 300 ml narrow-necked conical beaker. Moisten with 5 ml of water.

Add cautiously 15 ml of the saturated solution of potassium chlorate in nitric acid (4.18) and place the conical beaker on the hotplate and heat gently until all nitrogen oxides are expelled. Add 15 ml of dilute sulphuric acid (4.14) and heat the solution until strong white fumes have evolved, then cool.

If the residue appears dark (indicating the presence of carbon), slowly add a small amount of nitric acid (4.9) to the hot solution until the solution becomes colourless, then heat until strong white fumes have evolved.

Add 50 ml of water and bring to boil, then allow to cool at room temperature.

Filter the solution through an insoluble filter paper (5.4) in a 250 ml conical beaker. Wash the 300 ml conical beaker used to digest the sample and filter paper thoroughly with sulphuric acid (4.15) and collect the washing solutions in the same 250 ml conical beaker.

If acid insoluble material is present, then treat this residue as the procedure in 7.5, otherwise proceed to step 7.6.

In the case of lead concentrates, proceed to step 7.4.

7.4 Removal of lead sulfate

Quantitatively, transfer the precipitate into a 250 ml conical beaker with small amount of deionised water. Add 15 ml of ammonium acetate (4.19) and place the conical beaker on the hotplate and heat until dissolution of the $PbSO_4$.

Cool the solution to room temperature and filter through an insoluble filter paper (5.4), then wash the insoluble residue with sulphuric acid (4.15). Reject the filtrate and washing solution. If acid insoluble material is present, then treat this residue as the procedure in 7.5, otherwise proceed to step 7.6.

7.5 Dissolution of the insoluble residue

Quantitatively, transfer the acid insoluble residue into a 200 ml polytetrafluoroethylene beaker (5.5) with a small quantity of deionised water. Add 5 ml of nitric acid (4.9), 5 ml of dilute sulphuric acid (4.14), and 3 ml to 5 ml of hydrofluoric acid (4.16). Heat the solution until the evolution of white sulphuric acid fumes to remove silicon dioxide. Allow to cool, then dissolve the soluble salts with 10 ml of deionised water and 10 ml of nitric acid (4.9). Proceed to step 7.6.

7.6 Preparation of test solutions

Quantitatively, transfer the solution from step 7.5 and the filtrate from step 7.4 into a 200 ml volumetric flask and dilute to approximately 150 ml with deionised water. Allow this solution to cool in room temperature then dilute to 200 ml of water and mix well.

7.7 Preparation of calibration solutions

Using arsenic standard (4.21), prepare a series of calibration standards as per Table 1. Transfer the appropriate volumes of arsenic standard (4.21) using pipettes into 100 ml volumetric flasks containing the following:

a) 20 ml dilute sulphuric acid (4.14);

b) 10 ml nitric acid (4.9);

c) sufficient iron matrix/interference standard (4.3) to match the iron content of the samples;

If the iron content of the sample requires more than 30 ml of iron chloride solution to be added, change the concentration of the iron chloride solution (4.3) to ensure that the volume of iron chloride solution (4.3) does not exceed 30 ml.

d) sufficient matrix/interference standard to match the major element in the concentrate being measured. For copper sulfide concentrates, use copper matrix/interference standard (4.22). For zinc sulfide concentrates, use zinc matrix/interference standard (4.23). For lead sulfide concentrates, use lead matrix/interference standard (4.25). For nickel sulfide concentrates, use nickel matrix/interference standard (4.26).

Fill up nearly to the mark with water, mix, and equilibrate at room temperature then fill up exactly to the mark and mix again.

Table 1 — Calibrating solutions

Volume of arsenic standard ml	Arsenic mass μg	Concentration of arsenic μg/ml
0	0	0
0,5	100	1,0
1	200	2,0
2	400	4,0
5	1 000	10,0
10	2 000	20,0
20	4 000	40,0
30	6 000	60,0
35	7 000	70,0

7.8 Preparation of arsenic calibration curve

Set up the ICP-AES (5.3) according to the guidelines set out in 5.3. Adjust the instrument read-out scale to zero. Aspirate each calibration solution as prepared in step 7.7 through the ICP-AES and record the emission intensities. Manually or electronically plot a graph of the average emission intensities versus the mass of arsenic (in μg) and repeat errant standards if necessary.

Use ISO 8466-2 as a guide to determine the acceptability of the calibration curve.

7.9 Determination of arsenic content in test solutions

Immediately, after calibrating the ICP-AES (5.3), determine the arsenic content in the test solutions from step 7.7. Adjust the instrument read-out scale to zero. Aspirate the first duplicate of each sample through the ICP-AES and record the emission intensities checking the zero regularly.

Check the calibration of the instrument, then aspirate the second duplicate of each sample in the reverse order through the ICP-AES and record the emission intensities checking the zero regularly.

Determine the mass of arsenic in each test sample (F_{As}, in μg) from the curve determined in 7.9.

If more than 10 μg of arsenic is found for the blank test, then this shall be investigated and the results for the samples shall not be reported.

8 Expression of results

The mass fraction of arsenic in the test portion (w_{As}), expressed as a percentage, is given by the following formula:

$$w_{As} = \frac{F_{As} - F_{As\,blank}}{M \times 10^6} \times 100\,K \tag{1}$$

where

F_{As} is the mass of arsenic found in test sample aliquot, in μg;

$F_{As\,blank}$ is the mass of arsenic found in the blank test, in μg;

M is the mass of the test portion, in g.

K is the hygroscopic moisture conversion factor, calculated using the following formula:

$$K = 100 / (100 - H) \tag{2}$$

where

H is the hygroscopic moisture content of the sample, expressed as a percentage, determined using ISO 9599.

NOTE   If pre-dried test samples are used, $H = 0$.

9 Precision

9.1 Expression of precision

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

a) For copper sulfide concentrates:

$$s_r = 0,009\,1\bar{X} + 0,001\,9 \tag{3}$$

$$s_L = 0,086\,6\bar{X} - 0,007\,3 \tag{4}$$

b) For lead sulfide concentrates:

$$s_r = 0,008\bar{X} + 0,002 \tag{5}$$

$$s_L = 0,020\overline{X} + 0,002 \tag{6}$$

c) For zinc sulfide concentrates:

$$s_r = 0,006\overline{X} + 0,002 \tag{7}$$

$$s_L = 0,028\overline{X} + 0,002 \tag{8}$$

d) For nickel sulfide concentrates:

$$s_r = 0,0107\overline{X} + 0,0017 \tag{9}$$

$$s_L = 0,0584\overline{X} + 0,0009 \tag{10}$$

where

$\overline{X}$ is the mean mass fraction of arsenic in the sample, expressed as a percentage;

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

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

9.2 Method for obtaining the final result

Calculate the following quantities from the duplicate results x_1 and x_2 (%) and process according to the flowchart in Annex B.

a) Mean of duplicate results:

$$\overline{X} = \frac{x_1 + x_2}{2} \tag{11}$$

Within laboratory standard deviation [s_r, using Formula (3) for copper sulfide concentrates, Formula (5) for lead sulfide concentrates, Formula (7) for zinc sulfide concentrates, or Formula (9) for nickel sulfide concentrates].

b) Repeatability limit:

$$R = 2,8\,s_r \tag{12}$$

9.3 Between-laboratories precision

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

Calculate the following quantities:

a) Mean of final results:

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \tag{13}$$

Between-laboratories standard deviation (s_L) by substituting μ_{12} for $\overline{X}$ in using Formula (4) for copper sulfide concentrates, Formula (6) for lead sulfide concentrates, Formula (8) for zinc sulfide concentrates, and Formula (10) for nickel sulfide concentrates.

Within-laboratory standard deviation (s_r) by substituting μ_{12} for $\overline{X}$ in using Formula (3) for copper sulfide concentrates, Formula (5) for lead sulfide concentrates, Formula (7) for zinc sulfide concentrates, and Formula (9) for nickel sulfide concentrates.

b) Permissible tolerance:

$$P = 2,8 \times \sqrt{s_L^2 + \frac{s_r^2}{2}} \tag{14}$$

c) Range

$$E = |\mu_1 - \mu_2| \tag{15}$$

where

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

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

If E is $\leq P$, 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). When the precision has been confirmed, the final laboratory result can be compared with the certified value, A_c. There are two possibilities as follows:

a) $|\mu_c - A_c| \leq C$ \hfill (16)

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

b) $|\mu - A_c| > C$ \hfill (17)

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

where

μ_c is the final result, expressed as a percentage by mass of arsenic of the certified reference material;

A_c is the certified value, expressed as a percentage by mass of arsenic of the certified reference material;

C is a quantity, expressed as a percentage by mass of arsenic depending on the type of certified reference material used as defined in 9.4.2.

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

9.4.2.1 General

The reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:2006.

9.4.2.2 Reference material certified/characterized by inter-laboratory test programme

The quantity C (see 9.4.1), expressed as a percentage by mass of arsenic, is given by the following formula:

$$C = 2 \times \sqrt{s_L^2 + \frac{s_r^2}{n} + s^2(A_c)} \tag{18}$$

where

$s^2(A_c)$ is the variance of the certified value;

n is the number of replicate determinations.

9.4.2.3 Reference material certified/characterized by one laboratory

The quantity C (see 9.4.1), expressed as a percentage by mass of arsenic, is given by the following formula:

$$C = \sqrt{2\,s_L^2 + \frac{s_r^2}{n}} \tag{19}$$

It is recommended that this type of certified reference material should 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) a reference to this International Standard (i.e. ISO 13547-2);

b) identification of the sample;

c) mass fraction of arsenic in the sample, expressed as a percentage;

d) date on which the test was carried out;

e) any occurrences noticed during the determination which may have had an influence on the results.