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**Copper and nickel sulfide ores and concentrates — Determination of total chlorine content — Alkaline fusion and potentiometric titration method**

*Minerais et concentrés de sulfure de cuivre et de sulfure de nickel — Détermination de la teneur totale en chlore — Méthode par fusion alcaline et par titrage potentiométrique*

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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](http://www.iso.org/directives)).

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

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# Copper and nickel sulfide ores and concentrates — Determination of total chlorine content — Alkaline fusion and potentiometric titration method

**CAUTION** — The use of this document can involve hazardous materials, operations and equipment. This document does not purport to address all of the safety issues associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to its use.

## 1 Scope

This document specifies an analytical method for the determination of total chlorine content using alkaline fusion and potentiometric titration.

This method is applicable to copper and nickel sulfide ores and concentrates having chlorine content in the following ranges:

- a) Method 1: 80 µg/g to 4 300 µg/g
- b) Method 2: 70 µg/g to 4 300 µg/g

## 2 Normative references (standards.iteh.ai)

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. 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, zinc and nickel sulfide concentrates — Determination of hygroscopic moisture content of the analysis sample — Gravimetric method*

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

## 3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

## 4 Principle

The test portion is decomposed by fusion with a mixture of sodium carbonate and potassium carbonate or with a mixture of potassium nitrate and potassium hydroxide. The fusion mixture is dissolved in water and the sulfide contained is oxidized with hydrogen peroxide.

At the acid pH, the chloride content is determined by potentiometric titration with silver nitrate solution after a known addition of the analyte.

## 5 Reagents

During the analysis, use only reagents of recognized analytical reagent grade and water that conforms with grade 2 of ISO 3696. Particular care should be taken to ensure all reagents are high purity.

**5.1 Sodium carbonate** ( $\text{Na}_2\text{CO}_3$ ), high purity.

**5.2 Potassium carbonate** ( $\text{K}_2\text{CO}_3$ ), high purity.

**5.3 Potassium nitrate** ( $\text{KNO}_3$ ), high purity.

**5.4 Potassium hydroxide** ( $\text{KOH}$ ), high purity.

**5.5 Sodium chloride** ( $\text{NaCl}$ ), high purity.

**5.6 Sodium bromide** ( $\text{NaBr}$ ), high purity.

**5.7 Silver nitrate** ( $\text{AgNO}_3$ ), high purity.

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**5.8 Flux mixture.**

Mix one portion of anhydrous sodium carbonate ([5.1](#)) and one portion of potassium carbonate ([5.2](#)).

If the grain size of some reagent is significantly different from the other, a size reduction and homogenization could be necessary.

Preferably use anhydrous reagent.

**5.9 Methyl orange** ( $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3$ ), high purity.

**5.10 Nitric acid** ( $\text{HNO}_3$ ),  $\rho_{20} = 1,4$  g/ml, AR grade.

**5.11 Hydrogen peroxide** ( $\text{H}_2\text{O}_2$ ), 30 % purity.

**5.12 Nitric acid solution** ( $\text{HNO}_3$ ), volume fraction 1:1.

To a 1 000 ml volumetric flask add approximately 400 ml of deionized water and then 500 ml of concentrated nitric acid ([5.10](#)). Cool to room temperature, dilute to volume and homogenize.

**5.13 Sodium chloride solution** ( $\text{NaCl}$ ), 0,01 mol/l.

Weigh 0,584 4 g of sodium chloride ([5.5](#)), oven-dried at 105 °C for approximately 1 h, and transfer to a 50 ml beaker. Adjust the mass before weighing according to the purity of the reagent used (mass =  $0,584\ 4 \times 100/\text{purity}$ ). Transfer to a glass volumetric flask of 1 000 ml using deionized water. Dissolve, dilute to volume with deionized water and homogenize.

**5.14 Sodium bromide solution** (NaBr), 0,01 mol/l.

Weigh 1,028 9 g of sodium bromide (5.6), oven-dried at 105°C for approximately 1 h, and transfer to a 50 ml beaker. Adjust the mass to weigh according to the purity of the reagent used ( $m = 1,028\ 9 \times 100/\text{purity}$ ). Transfer to a glass volumetric flask of 1 000 ml using deionized water. Dissolve and dilute to volume with deionized water and homogenize.

**5.15 Methyl orange solution**, 0,1 % mass fraction.

Dissolve 0,5 g of methyl orange (5.9) into a 500 ml flask with deionized water.

**5.16 Deionized water.****5.17 Silver nitrate solution** (AgNO<sub>3</sub>), 0,01 mol/l.

Dissolve 1,698 7 g of silver nitrate (5.7) in 1 l of deionized water. Stir to dissolve and allow to cool. Standardize this solution as specified in 5.18.

Adjust the mass to weigh according to a purity of the reagent used ( $m = 1,698\ 7 \times 100/\text{purity}$ ).

This standard solution should be prepared at the same ambient temperature as that at which the determinations will be conducted.

**5.18 Standardization — Determination of the titration factor of the silver nitrate solution**

Add to three separate 250 ml beakers 2 ml of 0,01 mol/l sodium bromide solution (5.14) and 4 ml of 0,01 mol/l sodium chloride solution (5.13) and dilute to 200 ml with deionized water.

Add some drops of methyl orange solution (5.15) and adjust the pH with drops of nitric acid solution (5.12) until the colour changes from yellow to red. Add 2 ml extra.

Insert the electrode for chloride titration (6.12) in the titration solution, stir at a constant rate and wait about 3 min before titration.

Carry out the titration with 0,01 mol/l silver nitrate solution (5.17).

The end point ( $E$ ) is detected automatically by the potentiometric sensor. The first end point represents the consumption of silver nitrate solution (5.17) due to the bromide ion ( $E1$ ) and the second due to the chloride ion plus the bromide ion ( $E2$ ). Calculate the volumes due to only the titration of chloride to each replicate  $V_1$ ,  $V_2$  and  $V_3$  using Formulae (1) to (3):

$$V_1 = E2_1 - E1_1 \quad (1)$$

$$V_2 = E2_2 - E1_2 \quad (2)$$

$$V_3 = E2_3 - E1_3 \quad (3)$$

Calculate the standardization factors  $f_1$ ,  $f_2$  and  $f_3$  using Formulae (4) to (6):

$$f_1 = V_{\text{NaCl}}/V_1 \quad (4)$$

$$f_2 = V_{\text{NaCl}}/V_2 \quad (5)$$

$$f_3 = V_{\text{NaCl}}/V_3 \quad (6)$$

where  $V_{\text{NaCl}}$  is the volume of solution (5.13) added in ml, which in this case is equal to 4 ml.

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Calculate to four significant figures the mean standardization factor,  $f$ , for the silver nitrate standard solution, provided that the range of the values of  $f_1$ ,  $f_2$  and  $f_3$ , does not exceed 0,02. If this range is exceeded, repeat the standardization or preparation of solutions.

It is desirable that the titration factor is in the range 0,99 to 1,01.

Use this factor at expression of results (see [Clause 10](#)) to obtain the total chlorine content of the samples.

## 6 Apparatus

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

Use ordinary laboratory apparatus and the following:

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

**6.2 Glassware beakers**, 250 ml and 400 ml.

**6.3 Zirconium crucibles**, capacity of 80 ml with caps.

**6.4 Nickel crucibles**, capacity of 80 ml with caps (desirable).

**6.5 Weighing device**, capable of weighing the test sample and test portions to an accuracy of 0,000 1 g.

**6.6 Oven**, capable of being maintained at  $105\text{ °C} \pm 5\text{ °C}$ .

**6.7 Gas burner.**

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**6.8 Muffle furnace**, capable of being maintained at  $340\text{ °C} \pm 20\text{ °C}$  and  $800\text{ °C} \pm 50\text{ °C}$ .

**6.9 Magnetic stirrer with hot plate.**

**6.10 Filter paper**, sufficient retention capacity for filtration to clear solution.

**6.11 Potentiometric titrator**, commercially available.

**6.12 Silver electrode for chloride titration** (single-rod measuring cell).

## 7 Instrument operating parameters

Refer to the manufacturer's instructions for optimizing electrode and potentiometric titrator operation.

## 8 Sample

### 8.1 Laboratory sample

The laboratory sample shall be taken and prepared in accordance with the procedures described in ISO 12743.



## 8.2 Test sample

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

NOTE A test sample is not required if pre-dried test portions are used, see [Annex A](#).

## 9 Procedure

### 9.1 Number of blank testing

Carry out two blank tests in parallel with the analysis using the same quantities of all reagents but omitting the test sample as described in [9.3](#).

NOTE Blank tests in this method are used to subtract the known addition of bromide and chloride to the test samples.

### 9.2 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.

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### 9.3 Determination

#### 9.3.1 General

This item specifies two fusion methods for test sample preparation analysis: the decomposition of the test portion by fusion with a mixture of carbonate salts ([9.3.2](#)) or potassium salts ([9.3.3](#)). The choice of method depends on materials, reagents and time available for performing the procedure.

#### 9.3.2 Decomposition of the test portion by fusion with a mixture of carbonate salts

##### 9.3.2.1 Decomposition

Taking multiple increments, extract a representative test portion from the test sample. Weigh to the nearest 0,1 mg approximately 5 g of test sample.

Transfer the test portion to a zirconium crucible ([6.3](#)).

Add to the crucible 25 g of the flux mixture ([5.8](#)) and mix gently, taking care to avoid projections.

Cover with a cap.

Place the crucibles in a muffle furnace ([6.8](#)) at 800 °C. The zirconium crucibles may have a short shelf life when subjected to 800 °C.

After 20 min to 30 min of heating, remove each crucible individually and swirl well, spreading through the walls of the crucibles before the melt solidifies.

Place the crucibles in order on a metal or ceramic plate and allow to cool.

##### 9.3.2.2 Dissolution of the test sample

Wash the crucible outside with deionized water and place in a 400 ml beaker ([6.2](#)).

Add deionized water to the beaker until the crucible is submerged. Be careful not to exceed the 200 ml graduation of the beaker.

Insert a magnetic bar into the crucible.

Place the beaker containing the crucible in the magnetic stirrer with hot plate (6.9). Warm and stir gently overnight so that the residue is completely digested.

Allow to cool.

Transfer the entire contents of the crucible to a 250 ml volumetric flask (6.1) and wash well with deionized water. Be sure that no residue remains in the crucible.

Fill to the mark with deionized water and homogenize well.

Proceed with solids separation by filtration or centrifugation.

Take 100 ml from the liquid part of the sample using volumetric equipment and transfer to a 250 ml beaker (6.2).

### 9.3.3 Decomposition of the test portion by fusion with a mixture of potassium salts

#### 9.3.3.1 Decomposition

Place 4 g of potassium hydroxide (5.4) in a nickel crucible (6.4).

Taking multiple increments, extract a representative test portion from the test sample. Weigh to the nearest 0,1 mg approximately 2 g of test sample.

Transfer the test portion to the nickel crucible (6.4) containing potassium hydroxide (5.4).

Add to the crucible 2 g of potassium nitrate (5.3) and another 4 g of potassium hydroxide (5.4). Mix gently.

Provide pre-fusion in the gas burner (6.7) for approximately 60 seconds to obtain as homogeneous a mix as possible, taking care to avoid projections.

The addition of fluxes should be carried out immediately before performing the pre-fusion.

Place the crucibles in a muffle furnace (6.8) at 340 °C.

After 30 minutes of heating, remove each crucible individually and swirl well, spreading through the walls of the crucibles before the melt solidifies.

Place the crucibles in order on a metal or ceramic plate and allow to cool.

#### 9.3.3.2 Dissolution of the test sample

Wash the crucible outside with deionized water and place on a stable and clean surface.

Fill the crucible with deionized water and wait about 2 h for complete dissolution of the melt.

Multiple increments of water can be used to promote dissolution, if desired, to make the process faster.

Transfer, with the aid of a rubber tip, the entire contents of the crucible to a 200 ml volumetric flask (6.1). Wash well with deionized water. Be sure that no residue remains in the crucible.

Fill to the mark with deionized water and homogenize well.

Proceed with solids separation by filtration or centrifugation.

Take 100 ml from the liquid part of the sample using volumetric equipment and transfer to a 250 ml beaker (6.2).

### 9.3.4 Oxidation of sulfide

Slowly add 15 ml of 30 % hydrogen peroxide (5.11) in increments of 5 ml to the 250 ml beaker (6.2) with test sample and swirl gently to mix the contents.

Be careful to avoid losses in violent reactions that could occur with some samples.

Warm up for 1 h at about 100 °C, using moderate magnetic stirring. Cover with watch glass and boil until the final volume reduces to nearly 100 ml, increasing the temperature and maintaining moderate magnetic stirring.

Cool the solution.

Add some drops of methyl orange solution (5.15) and adjust the pH with drops of nitric acid solution (5.12) until the colour changes from yellow to red. Add 2 ml extra.

Boil for about 15 min to get rid of the bubbles formed in the solution, maintaining the moderate magnetic stirring.

If possible, use individual stirring and heating.

### 9.3.5 Preparation of solution for titration

If it is possible to see a residue in the 250 ml beaker (6.2), quantitatively transfer the solution to a 250 ml volumetric flask (6.1). If no residue is observed, continue with 9.3.6.

Make up to volume with deionized water and mix well.

Proceed with solids separation by filtration or centrifugation.

Take 200 ml from the liquid part of the sample using volumetric equipment and transfer to a 250 ml beaker (6.2).

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### 9.3.6 Potentiometric titration

#### 9.3.6.1 Titration of blank tests

Add to the beakers of blank tests without residue 2 ml of 0,01 mol/l sodium bromide solution (5.14) and 4 ml of 0,01 mol/l sodium chloride solution (5.13).

Dilute to approximately 200 ml with deionized water.

Place the electrode for chloride titration (6.12) in the solution, stir at a constant rate and allow about 3 min before titration.

Carry out the titration with 0,01 mol/l silver nitrate solution (5.17).

The use of a valve that doesn't permit return in the dosage unit, when dipping the same inside the sample solution, is very important for the analysis. Do not carry out the potentiometric titration without this valve.

The end point ( $E$ ) is detected automatically by a potentiometric sensor. The first end point represents the consumption of silver nitrate solution (5.17) due to the bromide ion ( $E1$ ) and the second due to the chloride ion plus the bromide ion ( $E2$ ).

Calculate the volumes, in millilitres, of silver nitrate solution (5.17) consumed,  $V_{\text{blk}}$ , due to only the titration of chloride to blank solutions, using Formulae (7) and (8):

$$V_{\text{blk1}} = E2_1 - E1_1 \quad (7)$$