INTERNATIONAL STANDARD

ISO

13312

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Iron ores — Determination of potassium — Flame atomic absorption spectrometric method

Minerais de fer — Dosage du potassium — Méthode par spectrométrie d'absorption atomique dans la flamme

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13312 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This second edition cancels and replaces the first edition (ISO 13312:1997), which has been technically revised. It has been updated to alter the manner in which precision data are presented.

Iron ores — Determination of potassium — Flame atomic absorption spectrometric method

WARNING — This International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. 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 flame atomic absorption spectrometric method for the determination of the mass fraction of potassium in iron ores.

This method is applicable to mass fractions of potassium between 0,002 5 % and 0,52 % in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

2 Normative references

The following referenced documents are indispensable for the application 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 648, *Laboratory glassware — One-mark pipettes*

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

ISO 3082, *Iron ores — Sampling and sample preparation procedures*

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

ISO 7764, *Iron ores — Preparation of predried test samples for chemical analysis*

ISO 11323, *Iron ore and direct reduced iron — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11323 apply.

4 Principle

The test portion is decomposed by treatment with hydrochloric acid and hydrofluoric acid, followed by evaporation to dryness. The residue is wetted and the evaporation is repeated with a new portion of hydrochloric acid. The residue is dissolved with hydrochloric acid followed by appropriate dilution. The solution is aspirated into the air/acetylene flame of the atomic absorption apparatus.

The absorbance value obtained for potassium is measured in comparison with those obtained from calibration solutions.

5 Reagents

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

Reagents are to be selected or purified for the lowest possible blank value.

5.1 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

5.2 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (*m/m*), or ρ 1,19 g/ml, 48 % (*m/m*).

5.3 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 1 + 2.

5.4 Background solution

Dissolve 43 g of high-purity iron oxide powder[1] in 500 ml of hydrochloric acid (5.1). Allow to cool and dilute with water to 1 000 ml.

5.5 Potassium, standard solution, 20 µg K/ml.

Pulverize about 3 g of high-purity potassium chloride in an agate mortar, dry in an oven at 105 °C to 110 °C for 2 h, and allow to cool to room temperature in a desiccator. Dissolve 1,907 g in water, dilute with water to 1 000 ml in a volumetric flask and mix.

Transfer[2] 10,0 ml of this solution to a 500 ml volumetric flask, dilute with water to volume and mix.

Store this standard solution in a plastic bottle.

1 ml of this standard solution contains 20 µg of potassium.

6 Apparatus

Ordinary laboratory equipment, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042 respectively, and the following.

6.1 Polytetrafluoroethylene (PTFE) beakers, of capacity 100 ml, provided with PTFE covers.

6.2 PTFE-coated magnetic stirring bars.

6.3 PTFE digestion bomb.

6.4 Plastic pipettes.

6.5 Plastic volumetric flasks and storage bottles.

6.6 Magnetic stirring hotplates.

NOTE   Platinum vessels may be used instead of PTFE beakers.

Except where stated, glass equipment should be avoided, as it could contaminate the solutions.

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1) Instead of iron oxide, the use of metallic iron with a suitable oxidant is permitted. (The alkali content of the oxidant shall be low.)

2) Glass equipment may be used.

To obtain reliable values, the equipment should be cleaned and checked as follows.

a) Rinse all volumetric ware, including the pipettes used for preparing the calibration solutions, with dilute hydrochloric acid (5.3) before use. Check the calibration regularly or as needed.

b) Clean PTFE vessels and stirring bars by stirring with 50 ml of dilute hydrochloric acid (5.3) and by heating for 15 min. Discard the rinsings and conduct a blank test in each vessel in turn, exactly as specified in 8.3. If any absorbance value is above the limit specified in 8.3, the cleaning procedure should be repeated or acid reagents of a higher purity should be used. At no stage should the stirring bars be handled with the fingers.

c) Platinum vessels, exclusively used for potassium analysis according to this International Standard, can be cleaned by the same method as the PTFE vessels [see b)]. Otherwise, they should be pre-cleaned by fusion with lithium tetraborate or lithium borate, until the absorbance readings fall to those for the lithium salt alone.

d) Rinse storage bottles with dilute hydrochloric acid (5.3) before use.

6.7   Atomic absorption spectrometer.

WARNING — Follow the manufacturer's instructions for igniting and extinguishing the air/acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the burner is in operation.

The atomic absorption spectrometer shall meet the following criteria.

a) Minimum sensitivity: the absorbance of the most concentrated calibration solution (see 8.4.3) shall be at least 0,25.

b) Graph linearity: the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 of the value of the slope for the bottom 20 % of the concentration range determined in the same way.

c) Minimum stability: the standard deviation of the absorbance of the most concentrated calibration solution and that of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, shall be less than 1,5 % and 0,5 %, respectively, of the mean value of the absorbance of the most concentrated calibration solution.

The use of a strip-chart recorder and/or digital readout device is recommended to evaluate criteria a), b) and c) and for all subsequent measurements.

NOTE   Instrument parameters will vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. Solutions were aspirated into an air/acetylene flame of a premix burner.

— hollow cathode lamp, mA   10

— wavelength, nm   766,5

— air flow-rate, l/min   10

— acetylene flow-rate, l/min   2

In systems where the values shown for gas flow-rates do not apply, the ratio of the gas flow-rates may still be a useful guideline.

7 Sampling and samples

7.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 µm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores having significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

NOTE   A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

7.2 Preparation of predried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a manner that it is representative of the whole contents of the container. Dry the test sample at 105 °C ± 2 °C as specified in ISO 7764. (This is the predried test sample.)

8 Procedure

8.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with Annex A, independently, on one predried test sample.

NOTE   The expression "independently" means that the second and any subsequent result are not affected by the previous result(s). For the particular analytical method, this condition implies that the repetition of the procedure is carried out either by the same operator at a different time or by a different operator including, in either case, appropriate recalibration.

8.2 Test portion

Taking several increments, weigh, to nearest 0,000 2 g, 0,2 g to 0,5 g (depending on the potassium concentration) of the predried test sample obtained in accordance with 7.2.

The test portion should be taken and weighed quickly to avoid reabsorption of moisture.

8.3 Blank test and check test

Before proceeding to the treatment of test portions, ensure that the cleaning procedures conducted in 6.6 (see list items), together with the quality of the reagents being used, have produced a blank test value for the potassium determination not greater than the equivalent of 0,002 % (mass fraction) potassium in the ore.

In each run, one blank test and one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample(s) under the same conditions. A predried test sample of the certified reference material shall be prepared as specified in 7.2.

Where the analysis is carried out on several samples at the same time, the blank value may be represented by one test, provided that the procedure is the same and the reagents are from the same reagent bottles.

Where the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

The certified reference material should be of the same type as the sample to be analysed and the properties of the two materials should be sufficiently similar to ensure that, in either case, no significant changes in the analytical procedure will become necessary. Where a certified reference material is not available, a reference material may be used (see 9.2.4).

8.4   Determination

To prevent contamination during analysis, the following precautions shall be taken:

a)   finger contact with sample, solutions and stirring bars shall be avoided;

b)   mouth suction of pipettes shall not be permitted.

8.4.1   Decomposition of the test portion

Transfer the test portion (8.2) to a 100 ml PTFE beaker (6.1)[3]. Moisten it with a few drops of water, then add 10 ml of hydrochloric acid (5.1) and 10 ml of hydrofluoric acid (5.2). Add a PTFE-coated magnetic stirring bar (6.2) and cover with a PTFE cover. Adjust the temperature of the magnetic stirring hotplate (6.6) so that a temperature of about 98 °C will be maintained in water in a covered PTFE beaker. Heat, with stirring, for 45 min or until no further dissolution of the test portion occurs. Remove the cover, stop the stirrer, leaving the bar in the solution, and evaporate to dryness. Add 5 ml of hydrochloric acid (5.1) and evaporate again to dryness. Dissolve the salts in 5 ml of hydrochloric acid (5.1) and 40 ml of water, and transfer to a 100 ml one-mark plastic volumetric flask (6.5). Dilute to volume with water and mix.

NOTE   If any significant amount of residue remains, conduct the digestion process in a stirred PTFE digestion bomb (6.3) for 45 min at 160 °C.

8.4.2   Treatment of the solution

If the concentration of potassium is too high, it is necessary to dilute the test solution. Transfer, using a plastic pipette (6.4), y ml of the test solution to a 100 ml one-mark plastic volumetric flask, add $0{,}1 \times (100 - y)$ ml of the background solution (5.4), dilute with water to volume and mix (see Table 1).

A diluted test solution shall be measured together with a diluted blank test solution, containing the same amount of background solution as the test solution. Prepare the diluted blank test solution as follows: pipette y ml of the blank test solution into a 100 ml one-mark plastic volumetric flask, add $0{,}1 \times (100 - y)$ ml of the background solution, dilute to volume with water and mix.

Table 1 — Dilution guide for test solution

Potassium mass-fraction range %	Aliquot from 100 ml y
0,002 to 0,060	—
0,060 to 0,20	30,0
0,20 to 0,60	10,0
0,60 to 1,00	5,0

8.4.3   Preparation of the set of calibration solutions

From the potassium standard solution (5.5), prepare calibration solutions as follows:

Using plastic pipettes, transfer 0 ml; 2,0 ml; 5,0 ml; 10,0 ml; 15,0 ml of potassium standard solution (5.5), respectively, to 100 ml one-mark plastic volumetric flasks. Add, using a plastic pipette, 10 ml of the background solution (5.4) to each, dilute with water to volume and mix. These calibration solutions cover the concentration range 0 µg K/ml to 3 µg K/ml and contain 3 000 µg Fe/ml.

Store the calibration solutions in plastic bottles.

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3)   See note in 6.6.

8.4.4 Adjustment of atomic absorption spectrometer

Optimize the response of the instrument as specified in 6.7. Set the wavelength of potassium (766,5 nm) to obtain minimum absorbance. After 10 min preheating of the burner, adjust the fuel flow and burner position to obtain maximum absorbance, while aspirating the most concentrated calibration solution (see 8.4.3). Aspirate water and the calibration solution to establish that the absorbance reading is not drifting, and then set the reading for water to zero absorbance.

8.4.5 Atomic absorption measurements

Aspirate the calibration and test solutions or diluted test solutions in order of increasing absorption, starting with the blank test solution, or diluted blank test solution, and the zero calibration solution. When a stable response is obtained for each solution, record the readings. Aspirate the test solutions or diluted test solutions at the proper points in the calibration series and record their readings. Aspirate water between each calibration and test solution. Repeat the measurements at least twice.

Obtain the net absorbance of each calibration solution by subtracting the average absorbance of the zero calibration solution. In a similar manner, obtain the net absorbance of the test solution or diluted test solution by subtracting the absorbance of the corresponding blank test solution.

Prepare calibration graphs by plotting the net absorbance values of the calibration solutions against the concentration, in micrograms of potassium per millilitre (the test solution or, if diluted, the diluted test solution is the final test solution).

Convert the net absorbance of the final test solution to micrograms of potassium per millilitre by means of the calibration graph.

With concentration readings, the calculation should be made from absorbances to permit checking of the graph's linearity and the blank test value.

9 Expression of results

9.1 Calculation of mass fraction of potassium

The mass fraction of potassium, expressed as a percentage, is calculated to five decimal places for mass fractions higher than 0,01 %, and to six decimal places for mass fractions lower than 0,01 %, using the equation

$$w_K = \frac{\rho_M}{m_1 \times 100}$$

(1)

where

w_K is the mass fraction of potassium, expressed as a percentage, of the test sample;

ρ_M is the concentration, in micrograms per millilitre, of potassium in the final test solution;

m_1 is the mass, in grams, of test sample represented in 100 ml of the final test solution (8.4.5), calculated from the equation

$$m_1 = \frac{m \times V}{100}$$

     m being the mass, in grams, of the test portion (8.2);

     V being the volume, in millilitres, of the aliquot taken in 8.4.2. If no dilution has been made, $V = 100$.

9.2 General treatment of results

9.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equations[4)]

$$R_{\mathrm{d}} = 0,024\,3\,X^{0,5653} \tag{2}$$

$$P = 0,044\,0\,X^{0,5908} \tag{3}$$

$$\sigma_{\mathrm{d}} = 0,008\,6\,X^{0,5653} \tag{4}$$

$$\sigma_{\mathrm{L}} = 0,014\,3\,X^{0,5969} \tag{5}$$

where X (i.e. w_{K}) is calculated as follows:

— for the within-laboratory Equations (2) and (4), the arithmetic mean of the duplicate values;

— for the between-laboratories Equations (3) and (5), the arithmetic mean of the final results (9.2.5) of the two laboratories;

R_{d} is the independent duplicate limit;

P is the permissible tolerance between laboratories;

σ_{d} is the independent duplicate standard deviation;

σ_{L} is the between-laboratories standard deviation.

9.2.2 Determination of analytical result

Having computed the independent duplicate results according to Equation (1), compare them with the independent duplicate limit (R_{d}), using the procedure given in Annex A, and obtain the final laboratory result μ (see 9.2.5).

9.2.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the same procedure as described in 9.2.2.

Compute the following quantity:

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \tag{6}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

μ_{12} is the mean of the final results.

Substitute μ_{12} for X in Equation (3) and calculate P.

If $|\mu_1 - \mu_2| \leqslant P$, the final results are in agreement.

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4)   Additional information is given in Annexes B and C.

9.2.4 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM) (see last paragraph of 8.3). Calculate the analytical result (μ_c) for the RM/CRM using the procedures in 8.1 and 8.2, and compare it with the reference or certified value A_c. There are two possibilities:

a) $\left| \mu_c - A_c \right| \leqslant C$ in which case the difference between the reported result and the reference/certified value is statistically insignificant.

b) $\left| \mu_c - A_c \right| > C$ in which case the difference between the reported result and the reference/certified value is statistically significant.

where

μ_c is the analytical result for the certified reference material;

A_c is the certified/reference value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:2006, *Reference materials — General and statistical principles for certification*.

For a CRM certified by an interlaboratory test programme

$$ C = 2 \left[\sigma_L^2 + \frac{\sigma_d^2}{n} + V(A_c) \right]^{1/2} $$

where

$V(A_c)$ is the variance of the certified value A_c (= 0 for a CRM certified by only one laboratory);

n is the number of replicate determinations carried out on the CRM/RM.

A CRM certified by only one laboratory should be avoided unless it is known to have an unbiased certified value.

9.2.5 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operations specified in Annex A, calculated to five decimal places for mass fractions of potassium higher than 0,01 %, and to six decimal places for mass fractions lower than 0,01 %. For mass fractions higher than 0,01 %, the value is rounded off to the third decimal place as specified in a), b) and c). In a similar manner, with the ordinal numbers increased by one, the value for mass fractions lower than 0,01 % is rounded off to the fourth decimal place.

a) If the figure in the fourth decimal place is less than 5, it is discarded and the figure in the third decimal place is kept unchanged.

b) If the figure in the fourth decimal place is 5 and there is a figure other than 0 in the fifth decimal place, or if the figure in the fourth decimal place is greater than 5, the figure in the third decimal place is increased by one.

c) If the figure in the fourth decimal place is 5 and the figure 0 is in the fifth decimal place, the 5 is discarded and the figure in the third decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and is increased by one if it is 1, 3, 5, 7 or 9.

9.3 Oxide factor

The oxide factor, expressed as a percent, is given by the following equation:

$$w_{K_2O} = 1{,}204\ 6 \times w_K$$

10 Test report
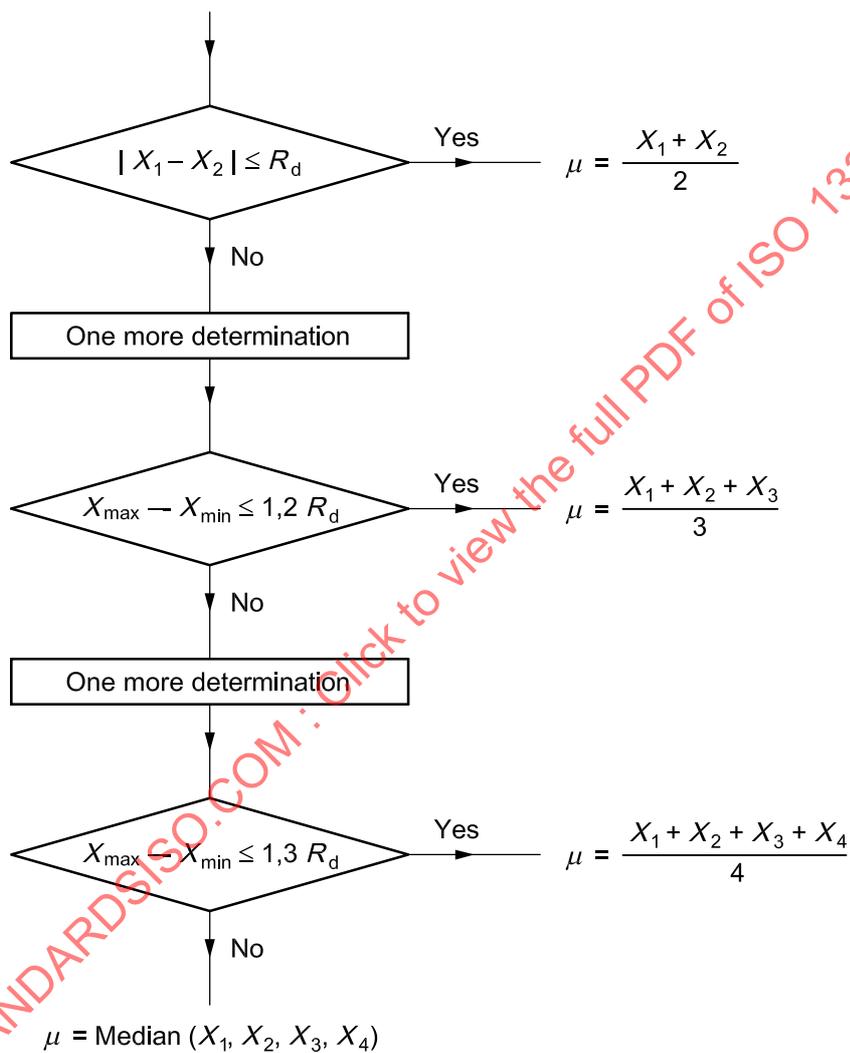
The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) a reference to this International Standard;

d) details necessary for the identification of the sample;

e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination and any operations not specified in this International Standard which may have had an influence on the results, either for the test sample or for the certified reference material(s).

Annex A
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples

Start with independent duplicate results

$|X_1 - X_2| \leq R_d$ — Yes — $\mu = \dfrac{X_1 + X_2}{2}$

No

One more determination

$X_{max} - X_{min} \leq 1{,}2\, R_d$ — Yes — $\mu = \dfrac{X_1 + X_2 + X_3}{3}$

No

One more determination

$X_{max} - X_{min} \leq 1{,}3\, R_d$ — Yes — $\mu = \dfrac{X_1 + X_2 + X_3 + X_4}{4}$

No

$\mu = \text{Median}\,(X_1, X_2, X_3, X_4)$