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Aluminium ores — Determination of vanadium content — BPHA spectrophotometric method

*Minerais alumineux — Dosage du vanadium — Méthode spectrophotométrique
au BPHA*



Reference number
ISO 9208 : 1989 (E)

Foreword

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International Standard ISO 9208 was prepared by Technical Committee ISO/TC 129, *Aluminium ores*.

Annex A forms an integral part of this International Standard. Annex B is for information only.

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Aluminium ores — Determination of vanadium content — BPHA spectrophotometric method

1 Scope

This International Standard specifies a BPHA spectrophotometric method for the determination of the vanadium content of aluminium ores. It is applicable to ores containing between 0,005 % (m/m) and 0,4 % (m/m) of vanadium pentoxide.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5725 : 1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

ISO 8558 : 1985, *Aluminium ores — Preparation of pre-dried test samples.*

3 Principle

Decomposition of the test portion by sintering followed by a brief fusion with sodium peroxide. Dissolution of the melt in water and removal of titanium and iron by filtration of the resultant hydrous oxides. Acidification and dilution of the filtrate. Measurement of an aliquot and oxidation of all the vanadium to the pentavalent state with potassium permanganate. Solvent extraction of the vanadium into chloroform as the *N*-benzoyl-*N*-phenylhydroxylamine complex from hydrochloric acid solution. Determination of the vanadium content of the extract by spectrophotometry.

4 Reagents

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

4.1 Sodium peroxide.

Use only the dry, free-flowing, off-white to pale yellow granules or powder.

WARNING — Sodium peroxide must be protected against humidity and must not be used once it has begun to agglomerate.

4.2 Iron(III) oxide, powder [$<0,001$ % (m/m) V_2O_5].

4.3 Sodium sulfate, 10 g/l solution.

Dissolve 10 g of the anhydrous salt in 1 litre of water.

4.4 Sodium sulfite, 30 g/l solution.

Dissolve 30 g of anhydrous sodium sulfite in 1 litre of water.

This solution should be freshly prepared on the day of use.

4.5 Sulfuric acid (ρ_{20} 1,84 g/ml), diluted 1 + 1.

4.6 Potassium permanganate, 1 g/l solution.

4.7 *N*-benzoyl-*N*-phenylhydroxylamine (BPHA), 2,5 g/l solution in chloroform.

This solution is stable for several months if stored in a glass container and kept in a cool, dark place. The presence of 1 % (V/V) to 2 % (V/V) ethanol as stabilizer in chloroform has no deleterious effect.

WARNING — The reagent *N*-benzoyl-*N*-phenylhydroxylamine is reported to be carcinogenic by skin absorption.

4.8 Chloroform, washed and dried.

Extract one volume of chloroform three times with equal volumes of water. Dry over anhydrous sodium sulfate in a glass container.

Prepare fresh daily.

4.9 Hydrochloric acid, ρ_{20} between 1,16 g/ml and 1,19 g/ml [about 32 % (m/m)], chilled to less than 5 °C.

NOTE — The absorbance of the vanadium-BPHA complex is slightly dependent upon the concentration of hydrochloric acid. Therefore, the same bottle of hydrochloric acid should be used for both the calibration and test solutions.

4.10 Vanadium, standard solution corresponding to 1,000 0 g of V_2O_5 per litre.

Dissolve 1,286 4 g of ammonium metavanadate (NH_4VO_3) in approximately 900 ml of water. Transfer to a 1 000 ml volumetric flask, dilute to the mark and mix.

1 ml of this standard solution corresponds to 1,000 0 mg of V_2O_5 .

4.11 Vanadium, standard solution corresponding to 80 mg of V_2O_5 per litre.

Transfer 20,00 ml of the standard vanadium solution (4.10) to a 250 ml volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution corresponds to 80 μ g of V_2O_5 .

4.12 Matrix solution.

Dissolve 41 g of sodium hydroxide (NaOH) in approximately 350 ml of water. Cool and cautiously add 72 ml of sulfuric acid (4.5). Cool and dilute to 500 ml with water.

5 Apparatus

Ordinary laboratory glassware and apparatus and

5.1 Dishes and lids of inert material, of sufficient size to take the required quantity of sample at a layer density of 5 mg/mm².

5.2 Muffle furnace, adjustable from 480 °C to 500 °C.

5.3 Zirconium, corundum or glassy carbon crucibles, 40 ml to 50 ml capacity.

5.4 Beakers, of nickel or polytetrafluoroethylene, of capacity 400 ml.

5.5 Separating funnels, 125 ml, of borosilicate glass with inert plastics stopcock and stopper. Before use, moisten the stopcock and stem of the funnel with a few drops of washed chloroform (4.8). Moisten the ground joint of the funnel with a few drops of water before stoppering.

5.6 Spectrophotometer, suitable for measurement of absorbance at about 530 nm.

5.7 Spectrophotometric cells, of 10 mm optical path length, with inert plastics stoppers in preference to lids. For absorbances less than 0,05, cells of longer optical path length shall be used.

6 Sampling and samples

6.1 Sampling

Laboratory samples shall be taken and crushed to pass a 150 μ m test sieve in accordance with the procedures specified in the relevant standards¹⁾.

6.2 Preparation of the test sample

Prepare the test sample by drying it in accordance with the procedure specified in ISO 8558.

7 Procedure

7.1 Number of determinations

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

NOTE — The expression "independently" implies a change of the person carrying out the analysis. If the same person carries out the analysis, the procedure should be repeated at a different time. In either case, appropriate recalibration should be undertaken.

7.2 Test portion

Weigh, to the nearest 0,1 mg, approximately 1 g of the test sample obtained in accordance with clause 6.

7.3 Blank test

In parallel with the decomposition of the test portion, prepare a blank solution according to the method of decomposition, but substituting 0,050 g of iron(III) oxide (4.2), for the test portion. When 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 used are from the same bottles.

7.4 Check test

In each run, one analysis of a certified reference material shall be carried out in parallel with the analysis of the ore sample(s) and under the same conditions.

1) Where no International Standards exist, the relevant standards shall be the national standards. Two International Standards on this subject are currently in preparation: ISO 8685, *Aluminium ores — Sampling procedures*, and ISO 6140, *Aluminium ores — Preparation of samples*.

NOTES

- 1 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 both cases no significant changes in the analytical procedure will become necessary.
- 2 The certified reference material is used only to validate the performance of the analytical procedure and not to adjust analytical results.

7.5 Determination**7.5.1 Decomposition of the test portion**

Transfer the test portion (7.2) to a dry crucible (5.3), add 10 g of the sodium peroxide (4.1) and mix intimately with a dry metal spatula. Place the crucible and contents in a muffle furnace (5.2), maintained at 480 °C to 500 °C for 45 min. Remove the crucible and contents from the furnace and heat over a burner to melt the sinter (about 30 s). Continue heating the molten state, while swirling, for a total time of 2 min.

7.5.2 Dissolution, removal of iron and titanium and preparation of the test solution

Place the cool crucible on its side in the beaker (5.4). Cautiously add 70 ml of water to the beaker behind the crucible. Remove the crucible and rinse into the solution in the beaker. Rinse the cover and the sides of the beaker, but keep the total volume to less than 100 ml. Cover the beaker and heat on a hotplate until the solution boils. Boil gently for 40 min while stirring frequently (see note 1). Remove from the heat, add 0,5 g of filter paper pulp, mix in thoroughly and allow the solids to settle for 2 min.

Filter through a 12,5 cm diameter, hardened, medium texture filter paper into a 400 ml glass beaker. Transfer the residue to the filter with the aid of a stream of hot sodium sulfate solution (4.3). Wash the residue at least 10 times with small portions of the wash solution (4.3), but keep the total volume to less than 200 ml. Discard the paper and residue.

Add 18 ml of sulfuric acid (4.5) to the filtrate, stir vigorously and cool (see note 2). Add potassium permanganate solution (4.6) dropwise until the pink colour persists for at least 2 min (see note 1).

Transfer the solution to a 250 ml volumetric flask, dilute to the mark with water and mix (see note 3). This is the test solution.

NOTES

- 1 30 min has been found to be the minimum requirement for the boiling period. Insufficient boiling may result in residual undecomposed peroxide requiring the addition of an excessive amount of potassium permanganate (> 1 ml) at a later step in the analysis. If a brown precipitate forms, the fusion and boiling steps should be repeated and the boiling time increased.
- 2 If the chromium content is known to be more than 0,05 % (*m/m*), add 1 ml of the sodium sulfite solution (4.4) (to reduce any yellow colour due to chromium) and add solution drop by drop until any yellow colour is discharged.
- 3 A small amount of white precipitate may settle out upon standing. This has been found to be innocuous and may be disregarded.

7.5.3 Spectrophotometric determination

Pipette 25,00 ml of the test solution into the prepared separating funnel (5.5). Add potassium permanganate solution (4.6) dropwise until the pink colour persists for at least 5 min. Perform the following steps upon each solution in turn:

- a) add 10 ml of BPHA solution (4.7);
- b) immediately add 20 ml of chilled hydrochloric acid (4.9);
- c) immediately extract vigorously for 30 s.

Allow the phases to separate for at least 10 min. Run the lower phase into a dry 25 ml volumetric flask. Add 10 ml of washed chloroform (4.8) to the separating funnel and extract for a further 30 s. Allow the phases to separate for at least 10 min, then combine the lower phase with the first extract. Dilute to the mark with washed chloroform and mix. Measure within 24 h, in a spectrophotometer (5.6), the absorbance of the test solution against washed chloroform in cells of optical path length 10 mm (5.7) at 530 nm and subtract the value obtained for the blank test solution (7.3).

7.6 Preparation of the calibration graph

Pipette 0 ml, 5,00 ml, 10,00 ml, 15,00 ml and 20,00 ml aliquots of the vanadium standard solution (4.11) into 100 ml volumetric flasks. For vanadium contents less than 0,05 % (*m/m*), use 0 ml, 1,00 ml, 2,00 ml, 5,00 ml and 10,00 ml aliquots. Add 50 ml of matrix solution (4.12), dilute to the mark with water and mix. Take 25,00 ml aliquots of these solutions through the same procedure as the test aliquot specified in 7.5.3. Plot the absorbance of each calibration solution against the respective mass, in micrograms, of vanadium pentoxide contained in the aliquots. [25 ml aliquots taken from dilutions of 5 ml, 10 ml, 15 ml and 20 ml aliquots of the vanadium standard solution (4.11) correspond respectively to 100 µg, 200 µg, 300 µg and 400 µg of vanadium pentoxide.]

NOTE — As a guide to the performance of the method the following information is provided.

The calibration solution containing 400 µg of V₂O₅, when measured at 530 nm using an optical path length of 10 mm and corrected for the zero calibration blank, gave an absorbance of 0,830.

8 Expression of results**8.1 Calculation of vanadium pentoxide content**

The vanadium content, expressed as a percentage by mass of vanadium pentoxide in the test sample is given by the formula

$$\frac{m_2}{m_1} \times \frac{250}{25} \times 10^{-4}$$

where

m_1 is the mass, in grams, of the test portion (7.2);

m_2 is the mass, in micrograms, of vanadium pentoxide contained in the aliquot of test solution (7.5.3), determined by using the calibration graph (7.6).

8.2 General treatment of results

8.2.1 Precision

A planned trial of this method was carried out by 10 laboratories at five levels of vanadium, each laboratory making two determinations at each level.

The results obtained were treated statistically in accordance with ISO 5725 and the resultant data are presented in table 1.

The data obtained showed a linear relationship between vanadium content, repeatability (r) and reproducibility (R) of the test results as summarized in table 1. Statistical data obtained on the NIST standard sample were not used in the regression analysis.

The graphical presentation of the precision data is given in annex B.

8.2.2 Acceptance of test results (see annex A)

The analytical values for the test sample shall be accepted when the analytical value obtained for the corresponding certified reference material agrees with the certified value within the limit of the value shown for R in table 1 and when the difference between the two values for the test sample does not exceed r , as calculated from the appropriate value of r given in table 1. When the difference exceeds the value of r , one or more additional tests shall be carried out in accordance with annex A, simultaneously with a corresponding blank test and an analysis of a certified reference material.

When the analytical value obtained for the certified reference material is outside the limits of the value shown for R in table 1, an additional analysis shall be carried out simultaneously on one test sample and one certified reference material, with one blank test. The analytical value obtained for the certified reference material shall be examined for the acceptance of the value for the test sample, as above. If the value obtained for the certified reference material is again outside the limits, the pro-

cedure shall be repeated with a different reference material of the same type of ore until two acceptable values for the test sample are obtained.

8.2.3 Calculation of final result

The final result is the arithmetical mean of the acceptable analytical values calculated to the fourth decimal place and rounded off to the second decimal place as follows:

- when the figure in the third decimal place is less than 5, it is discarded and the figure in the second decimal place is kept unchanged;
- when the figure in the third decimal place is 5 and there are figures other than 0 in the fourth decimal place, or when the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;
- when the figure in the third decimal place is 5 and there are no figures other than 0 in the fourth decimal place, the 5 is discarded and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8, and increased by one if it is 1, 3, 5, 7 or 9.

9 Test report

The test report shall include the following information:

- details necessary for the identification of the sample;
- reference to this International Standard;
- the result of the analysis;
- reference number of the result;
- any characteristics noticed during the determination and any operations not specified in this International Standard which may have had influence on the results either for the test sample or the certified reference material(s).

Table 1 — Precision data for vanadium determinations

Values in mass percentage

Sample	Ore type	Mean V_2O_5 content	Repeatability r	Reproducibility R
MT/12/3	Gibbsite/Boehmite/Hematite	0,024	0,003 1	0,006 1
MT/12/12	Diaspore [21,7 % (m/m) of Fe_2O_3 ; 4,0 % (m/m) of SiO_2]	0,053	0,003 7	0,006 6
NIST 696 ^{*)}	Gibbsite	0,069	0,003 8	0,010 1
MT/12/14	Boehmite/Kaolinite/Gibbsite [0,6 % (m/m) of Cr]	0,095	0,003 7	0,010 7
MT/12/15	Gibbsite [19,5 % (m/m) of Fe_2O_3]	0,284	0,013 8	0,020 4

^{*)} Certified value: 0,072 % (m/m) \pm 0,006 % (m/m)