# International Standard 7969

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# Manganese ores and concentrates — Determination of sodium and potassium contents — Flame atomic absorption spectrometric method

*Minerais et concentrés de manganèse — Dosage du sodium et du potassium — Méthode par spectrométrie d'absorption atomique dans la flamme*

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# Foreword

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International Standard ISO 7969 was prepared by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

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# Manganese ores and concentrates — Determination of sodium and potassium contents — Flame atomic absorption spectrometric method

## 1 Scope and field of application

This International Standard specifies a flame atomic absorption spectrometric method for the determination of sodium and/or potassium in manganese ores and concentrates.

The method is applicable to products having sodium contents from 0,02 to 1,0 % $(m/m)$, and potassium contents from 0,08 to 3,0 % $(m/m)$.

It should be read in conjunction with ISO 4297.

## 2 References

ISO 4296/1, *Manganese ores — Sampling — Part 1: Increment sampling.*

ISO 4296/2, *Manganese ores — Sampling — Part 2: Preparation of samples.*

ISO 4297, *Manganese ores and concentrates — Methods of chemical analysis — General instructions.*

## 3 Principle

In the case of ores which are easy to decompose, decomposition of a test portion by treatment with nitric, hydrofluoric and sulfuric acids. Removal of hydrofluoric acid by evaporation of the solution until the fumes of sulfuric acid disappear completely. Treatment of the solution with sulfuric acid and hydrogen peroxide to dissolve manganese dioxide.

In the case of ores which are difficult to decompose, decomposition of a test portion by treatment with hydrochloric, nitric, hydrofluoric and perchloric acids. Removal of hydrofluoric and perchloric acid by evaporation of the solution until fumes of perchloric acid disappear completely. Treatment of the solution with hydrochloric acid to dissolve manganese dioxide.

Addition of a caesium nitrate solution and appropriate dilution.

Aspiration of the solution into the flame of an atomic absorption spectrometer using an air/acetylene burner.

Comparison of absorbance values obtained for potassium and/or sodium with those obtained from calibration solutions.

## 4 Reagents

NOTE — Reagents are to be selected or purified for lowest possible blank values.

**4.1 Nitric acid,** $\varrho$ 1,40 g/ml.

**4.2 Hydrofluoric acid,** $\varrho$ 1,14 g/ml.

**4.3 Hydrochloric acid,** $\varrho$ 1,19 g/ml.

**4.4 Perchloric acid,** $\varrho$ 1,51 g/ml.

**4.5 Sulfuric acid,** $\varrho$ 1,84 g/ml, diluted 1 + 1.

**4.6 Hydrochloric acid** (4.3), diluted 1 + 2.

**4.7 Hydrogen peroxide,** 30 % $(m/m)$, free from alkali metals.

**4.8 Caesium nitrate,** 15 g/l solution.

**4.9 Iron,** 10 g/l background solution.

Dissolve 2,5 g of high-purity iron by adding 15 ml of the nitric acid (4.1) and 30 ml of water in a 400 ml beaker. Then add 15 ml of the sulfuric acid (4.5) and evaporate the solution to fumes of sulfuric acid, cool and transfer to a 250 ml one-mark volumetric flask, dilute with water to the mark and mix.

**4.10 Manganese,** 25 g/l background solution.

Dissolve 6,25 g of electrolytic manganese [purity 99,95 % $(m/m)$] by adding 30 ml of the hydrochloric acid (4.3) and 30 ml of water in a 400 ml beaker.

NOTE — Any slight surface oxidation on the electrolytic manganese shall be removed by rinsing in dilute hydrochloric acid, distilled water, and then in acetone prior to drying and weighing.

Add 35 ml of the sulfuric acid (4.5) and evaporate to fumes of sulfuric acid, cool and transfer to a 250 ml one-mark volumetric flask, dilute with water to the mark and mix.

**4.11 Potassium,** standard solution corresponding to 0,1 g of K per litre.

Dissolve 0,190 7 g of potassium chloride (dried at 110 °C to constant mass) in 200 ml of water in a 400 ml beaker. Transfer the solution into a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,1 mg of K.

Store this solution in a polyethylene bottle.

**4.12 Potassium,** standard solution corresponding to 0,01 g of K per litre.

Transfer 10 ml of potassium standard solution (4.11) to a 100 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,01 mg of K.

Store this solution in a polyethylene bottle.

**4.13 Sodium,** standard solution corresponding to 0,1 g of Na per litre.

Dissolve 0,254 2 g of the sodium chloride (dried at 110 °C to constant mass) in 200 ml of water in a 400 ml beaker. Transfer this solution into a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,1 mg of Na.

Store this solution in a polyethylene bottle.

**4.14 Sodium,** standard solution corresponding to 0,01 g of Na per litre.

Transfer 10 ml of sodium standard solution (4.13) to a 100 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,01 mg of Na.

Store this solution in a polyethylene bottle.

## 5 Apparatus

**5.1 Ordinary laboratory equipment,** and fluoroplastic beakers and covers, platinum or suitable platinum alloy dishes.

NOTES ON THE PREPARATION OF EQUIPMENT.

**5.1.1** Except where stated glass equipment shall be avoided as it could contaminate the solutions.

**5.1.2** The caps of the plastic bottles shall not be of a type which contains a separate wad insert. Such inserts usually contain a sodium compound which will contaminate the solution.

**5.1.3** In order to obtain reliable values the equipment shall be cleaned and checked as follows.

a) Rinse all volumetric ware including the pipettes used for preparing the calibration solutions with hydrochloric acid (4.6) before use. Check calibration regularly or as needed.

b) Clean fluoroplastic vessels by adding some hydrochloric acid (4.6) and heating for 15 min. Reject the rinsings and conduct a procedure in each vessel in turn as specified in 7.3. If any absorbance value is above the limit specified in 7.3 the cleaning procedure shall be repeated or acid reagents of a higher purity shall be used.

c) Platinum vessels used exclusively for alkali determinations shall either be cleaned by the same method as for fluoroplastic vessels, see b); or shall be precleaned by fusion with $Li_2B_4O_7$ or anhydrous $LiBO_2$ until the absorbance readings fall to those for the lithium salt alone.

d) Rinse storage bottles with hydrochloric acid (4.6) before use.

**5.2 Flame atomic absorption spectrometer,** equipped with an air/acetylene burner.

The atomic absorption spectrometer used in this method will be satisfactory if it meets the following criteria:

a) *minimum sensitivity:* the absorbance of the highest calibration solution shall be at least 0,25;

b) *graph linearity:* the slope of the calibration graph covering the top 20 % 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 % concentration range determined in the same way;

c) *minimum stability:* the standard deviation of the absorbance of the most concentrated calibration solution and the standard deviation of the absorbance 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 solution.

An atomic absorption spectrometer shall be preferably attached to a chart recorder and/or digital readout device. The following parameters can be used as guidelines. Solutions shall be aspirated into the air/acetylene flame.

| | Na | K |
|---|---|---|
| Hollow cathode lamp (mA) | 10 | 10 |
| High-frequency lamp (mA) | 80 to 100 | 80 to 100 |
| Wavelength (nm) | 589,0 | 766,5 |
| Air flow rate (l/min) | 10 | 10 |
| Acetylene flow rate (l/min) | 2 | 2 |

Table 1 — Dilution guide for test solution

| Expected content of sodium or potassium in sample | Aliquot portion | Background solution to be added | | Sodium or potassium content in the solution, measured |
|---|---|---|---|---|
| | | Manganese (4.10) | Iron (4.9) | |
| % (*m*/*m*) | ml | ml | ml | µg/ml |
| 0,02 up to 0,2 | — | — | — | 0,2 up to 2,0 |
| 0,2 up to 0,8 | 20 | 2 | 1 | 0,4 up to 1,6 |
| 0,8 up to 1,5 | 10 | 2 | 1 | 0,8 up to 1,5 |
| 1,5 up to 3,0 | 5 | 2 | 1 | 0,75 up to 1,5 |

## 6 Sampling

For the sampling of manganese ores, see ISO 4296/1. For the preparation of samples, see ISO 4296/2.

## 7 Procedure

**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 flame is burning.**

### 7.1 Test portion

Weigh 0,250 0 g of the test sample.

### 7.2 Blank test

Before proceeding to the treatment of the test portion, ensure that the cleaning procedure conducted in 5.1 together with the quality of the reagents being used have produced a blank value for the sodium and potassium determinations in each case not greater than the equivalent of 0,002 % alkali content in the ore. Carry out the blank test through all stages of the analysis.

### 7.3 Determination

### 7.3.1 Decomposition

**7.3.1.1** For materials easy to decompose

Transfer the test portion (7.1) to a platinum dish and dissolve in a mixture of 3 ml of the nitric acid (4.1), 5 ml of the hydrofluoric acid (4.2) and 5 ml of the sulfuric acid (4.5).

Evaporate the solution until the fumes of sulfuric acid appear and then cool. Wash the sides of the dish with water and evaporate until the fumes of sulfuric acid completely cease to evolve. Cool, wash down the sides of the dish with 10 to 15 ml of water, add 0,5 ml of the sulfuric acid (4.5), and 10 drops of the hydrogen peroxide (4.7). Heat the solution to dissolve manganese dioxide and to decompose the excess of hydrogen peroxide completely.

**7.3.1.2** For materials difficult to decompose

Transfer the test portion (7.1) to a 100 to 250 ml fluoroplastic beaker and dissolve in 10 ml of the hydrochloric acid (4.3). Then add 1 to 2 ml of the nitric acid (4.1) and 5 ml of the hydrofluoric acid (4.2). Add 5 ml of the perchloric acid (4.4), heat the solution until white fumes of perchloric acid appear and allow the solution to stand for 2 min.

Wash the sides of the beaker with distilled water and heat again until the fumes of perchloric acid disappear. Cool. Dissolve the residue in 10 ml of the hydrochloric acid (4.3) and, while heating, add 10 to 15 ml of water to dissolve the salts.

### 7.3.2 Preparation of the test solution

Transfer the solution (7.3.1) to a 250 ml one-mark volumetric flask, add 5 ml of the caesium nitrate solution (4.8), dilute to the mark with water and mix (test solution).

If the solution is turbid, filter it through a dry medium texture filter paper into a dry flask discarding the first portions of the filtrate. If the concentration of sodium or potassium is less than 0,2 % (*m*/*m*) use the entire test solution. If the concentration of sodium or potassium is more than 0,2 % (*m*/*m*) prepare a diluted test solution. Transfer an aliquot of the test solution (table 1) to a 100 ml one-mark volumetric flask, add iron (4.9) and manganese (4.10) background solutions in quantities according to table 1, add 2 ml of the caesium nitrate solution (4.8).

If the decomposition was carried out as indicated in 7.3.1.2, add 5 ml of hydrochloric acid (4.3). Dilute with water to the mark and mix.

### 7.4 Preparation of the set of calibrating solutions

### 7.4.1 Potassium and sodium calibration solutions

Into a series of five platinum dishes (decomposition according to 7.3.1.1), or fluoroplastic beakers (decomposition according to 7.3.1.2), transfer, by means of a pipette, 2,0; 5,0; 10,0; 15,0 and 20,0 ml of potassium (4.12) and sodium (4.14) standard solutions. Add 1 ml of iron background solution (4.9) and 2 ml of manganese background solution (4.10) to each.

Treat these solutions in the same way (7.3) as the test portion, using the appropriate method of decomposition (7.3.1.1 or 7.3.1.2), except that

a) in 7.3.1.1 (second paragraph) the quantity of sulfuric acid (4.5) is reduced from 0,5 to 0,2 ml and the quantity of hydrogen peroxide is reduced from 10 to 4 drops;

b) in 7.3.1.2 (second paragraph) the quantity of hydrochloric acid is reduced from 10 to 4 ml.

Transfer the solutions obtained to a series of five 100 ml one-mark volumetric flasks, add 2 ml of caesium nitrate solution (4.8) to each, dilute with water to the mark and mix.

These calibration solutions contain 0,2 - 0,5 - 1,0 - 1,5 and 2,0 µg of potassium and sodium per millilitre.

NOTE — The range of the elements which can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 5.2. For instruments with high sensitivity, smaller portions of the standard solution or a more diluted standard solution can be used.

#### 7.4.2 Zero calibration solution

Transfer 1 ml of iron background solution (4.9) and 2 ml of manganese background solution (4.10) to a platinum dish (decomposition according to 7.3.1.1), or fluoroplastic beaker (decomposition according to 7.3.1.2) and treat as in 7.4.1, starting from the third paragraph.

### 7.5 Calibration and determination

#### 7.5.1 Spectrometric measurements

Optimize the response of the instrument as described in 5.2. After 10 min preheating of the burner and obtaining a stable response, aspirate the test solution or the diluted test solution (7.3.2). Record the readings. Aspirate water after the test solution to obtain zero absorbance.

Repeat the measurements at least twice. Obtain the net absorbance of the test solution by subtracting the absorbance of the reagent blank solution.

Simultaneously with the analysis of the test solution, analyse the series of calibration solutions (7.4).

Convert the net absorbance values of the test solution to micrograms of Na and/or K per millilitre by means of the calibration graph (7.5.2).

For the determination of potassium and sodium content by the bracketing method, compare the absorbance of the test solution with the absorbance of two calibration solutions, the absorbance of one being not more than 10 % higher and the second not more than 10 % lower than the absorbance of the test solution.

#### 7.5.2 Plotting the calibration graph

Obtain the net absorbance of each calibration solution (7.4.1) by subtracting the average absorbance of the zero calibration solution (7.4.2).

Prepare calibration graphs, by plotting the net absorbance values of the calibration solutions against micrograms of Na and K per millilitre.

## 8 Expression of results

### 8.1 Calculation

The sodium and/or potassium content, expressed as a percentage by mass, is given by formula (1)

$$\frac{\varrho_0 V K \times 100}{m \times 10^6} = \frac{\varrho_0 V K}{m \times 10^4} \qquad \ldots \quad (1)$$

where

$\varrho_0$ is the concentration, expressed in micrograms per millilitre, of sodium or potassium in the test solution, obtained from the calibration graph or by equation (2);

$m$ is the mass, in grams, of the test portion represented in the final test solution;

$V$ is the volume, in millilitres, of the final test solution;

$K$ is the conversion factor for the expression of the potassium or sodium content on the dry basis.

The value of $\varrho_0$ for the bracketing method is given by equation (2)

$$\varrho_0 = \varrho_1 + \frac{(\varrho_2 - \varrho_1) \times (A_0 - A_1)}{A_2 - A_1} \qquad \ldots \quad (2)$$

where

$\varrho_1$ is the content, expressed in micrograms per millilitre, of potassium or sodium in the standard solution, the concentration of which is less than that of the test solution;

$\varrho_2$ is the content, expressed in micrograms per millilitre, of potassium or sodium in the standard solution, the concentration of which is higher than that of the test solution;

$A_0$ is the reading of the test solution, corrected for the reading of the blank solution;

$A_1$ is the reading of the standard solution containing iron and manganese and having concentration $\varrho_1$, corrected for the reading of the blank solution;

$A_2$ is the reading of the standard solution containing iron and manganese and having concentration $\varrho_2$, corrected for the reading of the blank solution.