International Standard 6127

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Chromium ores — Determination of phosphorus content — Reduced molybdophosphate photometric method

Minerais de chrome — Dosage du phosphore — Méthode photométrique au molybdophosphate réduit

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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It has been approved by the member bodies of the following countries :

Australia	France	Poland
Austria	Hungary	Romania
Bulgaria	India	South Africa, Rep of
China	Italy	United Kingdom
Czechoslovakia	Japan	USSR
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No member body expressed disapproval of the document.

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Chromium ores — Determination of phosphorus content — Reduced molybdophosphate photometric method

WARNING — Attention is drawn to the dangers involved in the use of some reagents (see the notes to sub-clauses 4.3 and 4.8).

1 Scope and field of application

This International Standard specifies a reduced molybdophosphate photometric method for the determination of the phosphorus content of chromium ores.

The method is applicable to products having a phosphorus content of 0,002 to 0,1 % (m/m).

This International Standard should be read in conjunction with ISO 6629.

2 Reference

ISO 6629, *Chromium ores and concentrates — Methods of chemical analysis — General instructions.*[1)]

3 Principle

Decomposition of a test portion, either

a) by treatment with nitric and perchloric acids, or

b) by fusion with sodium peroxide, followed by leaching with water.

Removal of chromium by distillation as chromyl chloride. Filtration of the residue. Removal of silicic acid by volatilization with nitric and hydrofluoric acids. Fusion of the residue with sodium carbonate or a mixture of sodium carbonate, sodium tetraborate and sodium nitrate; extraction of the fused melt with nitric acid and combining with the main solution.

Separation of phosphorus from chromium by co-precipitation with iron(III) hydroxide in ammoniacal solution.

Removal of arsenic by distillation as arsenic trichloride.

Formation of the yellow molybdophosphate complex, followed by its reduction to the blue complex with iron(II) ions in the presence of hydrochloric acid and hydroxylammonium chloride, by addition of iron(III) nitrate, ammonia, hydroxylammonium chloride, hydrochloric acid and ammonium molybdate solutions to an aliquot portion of the test solution.

Photometric measurement of the resultant complex using a spectrophotometer or photoelectric absorptiometer.

4 Reagents

4.1 Nitric acid, ϱ 1,40 g/ml.

4.2 Nitric acid, diluted 1 + 9.

4.3 Perchloric acid, ϱ 1,50 g/ml.

NOTE — Risk of poisoning by inhalation, swallowing or contact with the skin. Handle in an efficient fume cupboard, away from exposed flames, etc. Avoid inhalation of fumes and contact with skin, eyes and clothing.

4.4 Sodium peroxide, free from phosphorus.

4.5 Hydrochloric acid, ϱ 1,19 g/ml.

4.6 Hydrochloric acid, diluted 1 + 1.

4.7 Hydrochloric acid, diluted 1 + 100.

4.8 Hydrofluoric acid, 40 % (m/m) solution.

NOTE — Risk of poisoning by inhalation, swallowing or contact with the skin. Handle in an efficient fume cupboard, away from exposed flames, etc. Avoid inhalation of fumes and contact with skin, eyes and clothing.

1) At present at the stage of draft.

4.9 **Sodium carbonate**, anhydrous.

4.10 **Fusion mixture.**

Mix 100 g of the anhydrous sodium carbonate (4.9) with 50 g of the sodium tetraborate and 1 g of the sodium nitrate, and grind throughly in an agate or quartzite mortar.

4.11 **Iron(III) nitrate**, approximately 180 g/l solution.

Dissolve 180 g of iron(III) nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$], while heating, in 300 to 400 ml of water and add 5 ml of the nitric acid (4.1). Filter the solution into a 1 000 ml one-mark volumetric flask, cool, dilute to the mark and mix.

4.12 **Ammonia** solution, ϱ 0,91 g/ml.

4.13 **Ammonia** solution, diluted 1 + 1.

4.14 **Ammonia** solution, diluted 1 + 100.

4.15 **Hydroxylammonium chloride**, 30 % (m/m) solution.

4.16 **Ammonium molybdate**, $[(NH_4)_2MoO_4]$, 5 % (m/m) solution.

Prepare the solution using recrystallized ammonium molybdate and store in a quartz or polyethylene bottle. For recrystallization, dissolve 250 g of ammonium molybdate in 400 ml of water, while heating to 70 to 80 °C, filter the solution through a fine filter, and allow to cool to room temperature. Add, while stirring, 300 ml of ethyl alcohol rectified and allow the precipitate to settle for 1 h. Filter the precipitate by suction through a medium texture filter, placed in a Buchner funnel, wash with the ethyl alcohol 2 or 3 times and air dry.

NOTE — Commercially obtained reagent may be used without recrystallization if it does not contain compounds reducing to molybdenum blue.

4.17 **Ammonium bromide**, 10 % (m/m) solution.

4.18 **Phosphorus**, standard solution, corresponding to 0,01 g of P per litre.

Prepare from a standard phosphorus solution containing 0,1 mg of P in 1 ml.

For this purpose, dissolve 0,439 3 g of potassium dihydrogen phosphate (KH_2PO_4), dried to constant mass at 105 to 110 °C in 100 to 150 ml of water, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Transfer 50 ml of this standard phosphorus solution to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

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

5 Apparatus

Ordinary laboratory apparatus and

5.1 **Spectrophotometer** or **photoelectric absorptiometer.**

6 Procedure

6.1 Test portion

Weigh a mass of the test sample, chosen from table 1 in accordance with the expected phosphorus content.

Table 1

Expected phosphorus content		Mass of test portion	Volume of nitric acid (4.1)	Volume of perchloric acid (4.3)
% (m/m) from	to	g	ml	ml
0	0,015	1,0	5	70
0,015	0,05	0,50	5	50
0,05	0,10	0,20	5	30

6.2 Determination

6.2.1 Decomposition of test portion

6.2.1.1 Decomposition based on acid attack

Place the test portion (6.1) in a 250 ml beaker, moisten with water, add volumes of the nitric acid (4.1) and perchloric acid (4.3) as indicated in table 1, cover with a watch-glass, heat until the weak fuming of perchloric acid appears and then heat for a further 10 to 15 min.

Cool the contents of the beaker, wash it with water, evaporate until the weak fuming of perchloric acid appears and then heat for a further 10 to 15 min. Repeat this procedure to decompose the test portion completely.

Remove the bulk of chromium as chromyl chloride.

For this purpose, remove the watch-glass and carefully add the hydrochloric acid (4.5), drop by drop, along the walls of the beaker until brown fumes of chromyl chloride cease to evolve, chromium being reduced to the trivalent state. Replace the watch-glass on the beaker and continue to heat the solution to oxidize chromium completely.

Repeat the distillation of chromyl chloride to remove the bulk of chromium.

Allow the solution to cool, add 50 ml of hot water and heat to dissolve salts. Filter the solution through a medium-texture filter paper containing a small amount of ashless paper pulp, and wash the residue 12 to 15 times with hot hydrochloric acid (4.7) and 2 or 3 times with hot water. Collect the filtrate and washings in a 400 ml beaker and reserve as the main solution.

Keep the filter paper with the residue and continue according to 6.2.2.

6.2.1.2 Decomposition by alkaline fusion

Place the test portion (6.1) in a alumina, nickel or vitreous carbon crucible, add 6 to 8 g of the sodium peroxide (4.4), mix well using a glass rod, spread over 1 to 2 g of the sodium peroxide and fuse at 800 to 850 °C.

Allow the crucible to cool, place it in a 400 to 500 ml beaker, add 80 to 100 ml of water and cover the beaker with a watch-glass. After the violent reaction has ceased, boil the solution for 3 min and allow to cool. Add perchloric acid (4.3) to dissolve the precipitate of hydrates and then 5 ml in excess. Remove the crucible and rinse it with hot water. Evaporate the solution until the fumes of perchloric acid appear.

Remove the bulk of chromium as chromyl chloride according to 6.2.1.1.

Allow the solution to cool, add 50 ml of hot water and heat to dissolve salts. Filter the solution through a medium-texture filter paper containing a small amount of ashless paper pulp, and wash the precipitate 12 to 15 times with hot hydrochloric acid (4.7) and 2 or 3 times with hot water. Collect the filtrate and washings in a 400 ml beaker and reserve as the main solution.

Keep the filter paper with the residue and continue according to 6.2.2.

6.2.2 Treatment of residue

Transfer the residue from 6.2.1 with the filter in a platinum crucible, dry, ash the paper at a low temperature and ignite at 800 to 900 °C. Moisten the precipitate with water, add 4 or 5 drops of the nitric acid (4.1), 2 to 3 ml of the hydrofluoric acid (4.8), evaporate to dryness and ignite at 800 to 900 °C. Cool the crucible and fuse the residue with 1 to 2 g of the sodium carbonate (4.9) at 1 000 to 1 100 °C.

NOTE — In the case of ores which are difficult to decompose, fuse the residue with 2 g of the fusion mixture (4.10) at 1 000 to 1 100 °C.

Leach the melt while heating with 20 to 30 ml of the nitric acid (4.2) and combine with the main solution.

Add 1 ml of the iron(III) nitrate solution (4.11) to the solution, then add the ammonia solution (4.12) until a distinct ammoniacal smell persists, and heat the contents of the beaker to boiling. Allow the precipitate to settle for 2 to 3 min and filter it on a medium-texture filter paper. Wash the beaker and the precipitate on the filter 5 or 6 times with hot ammonia solution (4.14).

Wash the precipitate from the filter into the beaker in which the precipitation took place with hot water, wash the filter with 20 to 30 ml of hot hydrochloric acid (4.6) and 8 to 10 times with hot hydrochloric acid (4.7), collecting the washings in the same beaker. Evaporate to dryness.

To remove arsenic, add 10 ml of the hydrochloric acid (4.5) and evaporate the solution again to dryness. Dissolve the dry residue while heating in 25 ml of the hydrochloric acid (4.6), add 10 ml of the ammonium bromide solution (4.17) and evaporate the solution to dryness. Add 15 ml of the hydrochloric acid (4.5) and evaporate the solution again to dryness. Add 10 to 12 ml of the hydrochloric acid (4.5) and heat until the salts dissolve.

Transfer the solution to a 100 ml one-mark volumetric flask, cool, dilute to the mark and mix.

6.2.3 Preparation of solution for photometric measurement

Transfer 20 ml aliquot portions of the solution obtained to two 100 ml one-mark volumetric flasks, add to each flask 4 ml of the iron(III) nitrate solution (4.11) and the ammonia solution (4.13) until the first appearance of an iron(III) hydroxide precipitate. Add the hydrochloric acid (4.6), drop by drop, until the precipitate is dissolved.

Add 10 ml of the hydroxylammonium chloride solution (4.15), heat the solutions to boiling to decolorize them. If the yellowish colour of the solution persists, add 1 or 2 drops of the ammonia solution (4.13), and dissolve any turbidity which may appear by addition of 1 or 2 drops of the hydrochloric acid (4.6).

Allow the solutions to cool to 25 °C and add 11 ml of the hydrochloric acid (4.6).

Add, drop by drop, while stirring continuously, 8 ml of the ammonium molybdate solution (4.16) to one of the two volumetric flasks. Stir the solutions for 1 to 2 min, dilute to the mark with water and mix (the pH of these solutions should be 0,1 to 0,4).

6.2.4 Photometric measurement

Allow the solutions to stand for 10 min in order to develop the colour. Measure the absorbance of the test solution using the spectrophotometer (5.1) at 825 nm or the photoelectric absorptiometer (5.1), fitted with a red light filter (at a wavelength of 620 to 640 nm) in a 50 mm cell, against the solution containing no ammonium molybdate as reference.

6.2.5 Blank test

Carry out the blank test through all stages of the analysis.

6.2.6 Preparation of calibration graph

Transfer into six 100 ml one-mark volumetric flasks, using a microburette, 0,5 — 1,0 — 2,0 — 3,0 — 4,0 and 5,0 ml of the standard phosphorus solution (4.18), corresponding to 5 — 10 — 20 — 30 — 40 and 50 µg of phosphorus respectively. The seventh 100 ml one-mark volumetric flask serves for the blank determination.

Add to each flask 4 ml of the iron(III) nitrate solution (4.11), 20 ml of water and the ammonia solution (4.13) until a precipitate of iron(III) hydroxide appears. Add the hydrochloric acid (4.6), drop by drop, until the precipitate is dissolved. Add 10 ml of the hydroxylammonium chloride (4.15), heat the solutions to boiling to decolorize them. If the yellowish colour of the solution persists, add 1 or 2 drops of the ammonia solution

(4.13); dissolve any turbidity which may appear by addition of 1 or 2 drops of the hydrochloric acid (4.6). Allow the solutions to cool and add 11 ml of the hydrochloric acid (4.6). Add, drop by drop, 8 ml of the ammonium molybdate (4.16), while stirring continuously, stir the solutions for 1 to 2 min, dilute to the mark with water and mix.

Carry out the photometric measurements as specified in 6.2.4, against water as reference.

Prepare a calibration graph by plotting absorbance values (deducting the absorbance value of the solution containing no phosphorus) against the nominal phosphorus contents, of the solutions.

7 Expression of results

7.1 Calculation

Convert the absorbance reading for the test solution to phosphorus content by means of the calibration graph (6.2.6), deducting the absorbance reading for the blank test.

The phosphorus (P) content is given, as a percentage by mass, by the formula

$$\frac{m_1 \times 100}{m_2} \times K$$

where

m_1 is the mass, in grams, of phosphorus found in the aliquot portion of the test solution, after correction for the blank value;

m_2 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

K is the conversion factor for the expression of the phosphorus content on the dry basis.

7.2 Permissible tolerances on results of duplicate determinations

Table 2

Phosphorus content	Permissible tolerance
% (m/m)	% (m/m)
From 0,002 to 0,004	0,001
From 0,004 to 0,01	0,002
From 0,01 to 0,02	0,003
From 0,02 to 0,04	0,004
From 0,04 to 0,06	0,005
From 0,06 to 0,10	0,006