

International Standard



4937

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Steel and iron — Determination of chromium content — Potentiometric or visual titration method

Aciers et fontes — Dosage du chrome — Méthode par titrage potentiométrique ou visuel

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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4937 was prepared by Technical Committee ISO/TC 17, *Steel*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Steel and iron — Determination of chromium content — Potentiometric or visual titration method

1 Scope and field of application

This International Standard specifies a method for the determination of chromium in steel and iron by potentiometric or visual titration.

The method is applicable to chromium contents between 0,25 and 35 % (*m/m*).

If vanadium is present, the visual titration is applicable only to test portions containing less than 3 mg of vanadium.

2 References

ISO 377, *Wrought steel — Selection and preparation of samples and test pieces.*

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648, *Laboratory glassware — One-mark pipettes.*

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

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

3 Principle

Dissolution of a test portion with appropriate acids.

Oxidation of chromium in an acid medium to chromium(VI) by ammonium peroxydisulfate in the presence of silver sulfate. Reduction of manganese(VII) by hydrochloric acid.

Reduction of chromium(VI) by ammonium iron(II) sulfate standard solution.

In the case of potentiometric detection, determination of the equivalence point by measurement of the potential variation when the ammonium iron(II) sulfate standard solution is being added.

In the case of visual detection, titration of the excess ammonium iron(II) sulfate by potassium permanganate standard solution which also acts as the indicator.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity, free from oxidizing or reducing activity.

4.1 Urea.

4.2 Perchloric acid, ρ approximately 1,67 g/ml.

4.3 Hydrofluoric acid, ρ approximately 1,15 g/ml.

4.4 Orthophosphoric acid, ρ approximately 1,70 g/ml.

4.5 Nitric acid, ρ approximately 1,40 g/ml.

4.6 Hydrochloric acid, ρ approximately 1,19 g/ml, diluted 1 + 1.

4.7 Hydrochloric acid, ρ approximately 1,19 g/ml, diluted 1 + 10.

4.8 Sulfuric acid, ρ approximately 1,84 g/ml, diluted 1 + 1.

4.9 Sulfuric acid, ρ approximately 1,84 g/ml, diluted 1 + 5.

4.10 Sulfuric acid, ρ approximately 1,84 g/ml, diluted 1 + 19.

4.11 Silver sulfate, 5 g/l solution.

4.12 Ammonium peroxydisulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, 500 g/l solution.

Prepare this solution immediately before use.

4.13 Manganese sulfate $[\text{MnSO}_4 \cdot \text{H}_2\text{O}]$, 4 g/l solution.

4.14 Manganese sulfate $[\text{MnSO}_4 \cdot \text{H}_2\text{O}]$, 100 g/l solution.

4.15 Potassium permanganate, 5 g/l solution.

4.16 Sodium nitrite, 3 g/l solution.

Prepare this solution immediately before use.

4.17 Sulfamic acid $(\text{NH}_2\text{SO}_3\text{H})$, 100 g/l solution.

This solution remains stable for one week only.

ISO 4937-1986 (E)

4.18 Potassium permanganate, standard solution.**4.18.1 Preparation of the solution**

Dissolve 3,2 g of potassium permanganate in 1 000 ml of water. After storage in complete darkness for 2 weeks, filter through a thick fritted filter without washing. Keep the solution in a coloured glass bottle and avoid contact with organic matter.

4.18.2 Standardization of the solution

Boil 250 ml of sulfuric acid (4.10) in a 600 ml beaker for 10 min and allow to cool. Weigh, to the nearest 0,000 1 g, 0,300 0 g of sodium oxalate $[(\text{COONa})_2]$ previously dried at 105 °C and cooled in a desiccator. Dissolve the salt in boiled sulfuric acid (4.10). Add 39 to 40 ml of potassium permanganate solution (4.18.1) at a rate of 25 to 35 ml/min, stirring gently. The violet colour of the permanganate will disappear in approximately 45 s. Heat to 70 to 75 °C and complete the titration.

Towards the end, titrate very slowly and allow each drop to become colourless before adding the next.

To determine the blank test, titrate 250 ml of sulfuric acid (4.10), as described above, concurrently.

The concentration (c_2) of the potassium permanganate standard solution, expressed as milligrams of chromium per millilitre, is given by the formula

$$c_2 = \frac{300,0 \times 1,733}{6,700 \times (V_1 - V_0)}$$

where

V_1 is the volume, in millilitres, of potassium permanganate solution (4.18.1) used for titrating sodium oxalate;

V_0 is the volume, in millilitres, of potassium permanganate solution (4.18.1) used for titrating the blank test of sulfuric acid (4.10);

6,700 is the molar mass of sodium oxalate divided by 20;

1,733 is the mass, in milligrams, of chromium(VI) contained in 1 ml of the potassium dichromate standard reference solution (4.20);

300,0 is the mass, in milligrams, of sodium oxalate weighed.

4.19 Ammonium iron(II) sulfate $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$, standard solution in sulfuric acid medium.

1 ml of this solution corresponds to about 2 mg of chromium.

4.19.1 Preparation of the solution

Dissolve 46 g of ammonium iron(II) sulfate hexahydrate in about 500 ml of water, add 110 ml of sulfuric acid (4.8), cool, dilute to 1 000 ml and mix.

4.19.2 Potentiometric standardization of the solution (to be carried out just before use)

Take 30,0 ml of the potassium dichromate standard reference solution (4.20), transfer to a 600 ml beaker, add 45 ml of sulfuric acid (4.9) and make up to about 400 ml with water.

Titrate according to the conditions specified in 7.3.3.1.

The corresponding concentration (c_1) of ammonium iron(II) sulfate solution (4.19.1), expressed in milligrams of chromium per millilitre, is given by the formula

$$c_1 = \frac{30,0 \times 1,733}{V_2}$$

where

V_2 is the volume, in millilitres, of ammonium iron(II) sulfate solution (4.19.1) used for the standardization;

30,0 is the volume, in millilitres, of the potassium dichromate standard reference solution (4.20) taken for the standardization;

1,733 is the mass, in milligrams, of chromium contained in 1 ml of the potassium dichromate standard reference solution (4.20).

4.19.3 Visual standardization of the solution (to be carried out just before use)

Take 25,0 ml of ammonium iron(II) sulfate solution (4.19.1) and add 325 ml of sulfuric acid (4.10). Titrate using the potassium permanganate standard solution (4.18) until a slight violet colour persists.

To determine the blank test, titrate a mixture of 25 ml of water and 325 ml of sulfuric acid (4.10) using the potassium permanganate standard solution (4.18).

The corresponding concentration (c'_1) of the ammonium iron(II) sulfate standard solution (4.19), expressed in milligrams of chromium per millilitre, is given by the formula

$$c'_1 = c_2 \times \frac{V_3 - V_0}{25,0}$$

where

c_2 is the concentration of the potassium permanganate standard solution (4.18), expressed as milligrams of chromium per millilitre;

V_3 is the volume, in millilitres, of the potassium permanganate standard solution (4.18) used to oxidize 25 ml of ammonium iron(II) sulfate solution (4.19.1);

V_0 is the volume, in millilitres, of the potassium permanganate standard solution (4.18) used for titrating the blank test of sulfuric acid (4.10);

25,0 is the volume, in millilitres, of ammonium iron(II) sulfate solution (4.19.1) used for the standardization.

4.20 Potassium dichromate, standard reference solution.

Weigh, to the nearest 0,000 1 g, 4,903 1 g of potassium dichromate previously dried at 150 °C to constant mass and cooled in a desiccator.

Dissolve in water, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard reference solution contains 1,733 mg of Cr.

5 Apparatus

Ordinary laboratory apparatus (see the note) and

5.1 Potentiometric titration device, which permits a difference in potential to be measured with platinum-saturated calomel electrodes.

NOTE — All volumetric glassware shall be class A, in accordance with ISO 385/1, ISO 648 or ISO 1042 as appropriate.

6 Sampling

Carry out sampling in accordance with ISO 377 or the appropriate national standards for iron.

7 Procedure

WARNING: Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic material in general.

7.1 Test portion

According to the presumed chromium content, weigh, to the nearest 0,000 1 g, the following mass (*m*) of the test portion:

- for chromium contents between 0,25 and 2 % (*m/m*), *m* approximately 2 g;
- for chromium contents between 2 and 10 % (*m/m*), *m* approximately 1 g;
- for chromium contents between 10 and 25 % (*m/m*), *m* approximately 0,5 g;
- for chromium contents between 25 and 35 % (*m/m*), *m* approximately 0,25 g.

7.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, using the same reagents, as in the determination, but omitting the test portion.

7.3 Determination

7.3.1 Preparation of the test solution

7.3.1.1 Unalloyed steel and iron

Place the test portion (7.1) in a 600 ml beaker, add 60 ml of sulfuric acid (4.9) and 10 ml of orthophosphoric acid (4.4), and heat to dissolve, then oxidize with 15 ml of nitric acid (4.5). Heat until dense white fumes are given off, cool and then add 100 ml of water.

To accelerate the dissolution of a test portion which has a high silicon content, a few drops of hydrofluoric acid (4.3) may be added (see note 1).

7.3.1.2 Chromium and/or nickel alloyed steel and iron

Place the test portion (7.1) in a 600 ml beaker, add 25 ml of hydrochloric acid (4.6) and heat to dissolve, then oxidize with 15 ml of nitric acid (4.5). If dissolution proves to be particularly difficult, add 1 to 2 ml of hydrofluoric acid (4.3). Then add 20 ml of sulfuric acid (4.8) and 10 ml of orthophosphoric acid (4.4), and heat until dense white fumes appear.

After cooling, add a further 15 ml of nitric acid (4.5) to the fuming solution, if necessary making further additions, until the carbides have completely decomposed. Continue fuming to remove completely oxides of nitrogen then cool and add 100 ml of water (see note 1).

7.3.1.3 Steel containing tungsten

Place the test portion (7.1) in a 600 ml beaker, add 25 ml of hydrochloric acid (4.6) then 20 ml of sulfuric acid (4.8) and 10 ml of orthophosphoric acid (4.4) and heat until effervescence has ceased. If dissolution proves to be particularly difficult add 1 to 2 ml of hydrofluoric acid (4.3). Oxidize with 15 ml of nitric acid (4.5) then heat until dense white fumes appear.

After cooling, add a further 15 ml of nitric acid (4.5) to the fuming solution, if necessary making further additions, until the carbides have completely decomposed. Continue fuming to remove completely oxides of nitrogen then cool and add 100 ml of water (see note 1).

7.3.1.4 High alloyed steel and iron, or steel and iron with high silicon content

Place the test portion (7.1) in a 750 ml conical flask, and add 20 ml of hydrochloric acid (4.6), 10 ml of nitric acid (4.5) and 1 ml of hydrofluoric acid (4.3).

When effervescence has ceased, add 30 ml of perchloric acid (4.2). Heat until white fumes are given off, cover with a watch-glass and continue to heat until the alloy has completely dissolved (the white fumes being retained in the flask). Allow to cool.

Add 30 ml of water, boil for 5 min, and allow to cool (see note 1). Transfer quantitatively into a 600 ml beaker and add 20 ml of sulfuric acid (4.8), 10 ml of orthophosphoric acid (4.4) and 70 ml of water.

ISO 4937-1986 (E)

7.3.2 Oxidation of chromium and preparation for titration

If necessary, to remove graphite, filter the test solution through a cellulose-pulp-lined filter and wash with sulfuric acid (4.10). Dilute to about 350 ml with warm water, and add 20 ml of silver sulfate solution (4.11) and 10 ml of ammonium peroxydisulfate solution (4.12). Cover the beaker with a watch-glass and boil for 10 min (see note 2).

Then, break down the permanganic acid by adding to the solution, after it has been brought to the boil, firstly 15 ml of hydrochloric acid (4.7), then, after about 3 min, if necessary a further amount of hydrochloric acid (4.7), drop by drop, until the violet colour disappears (see note 3). Boil for 10 min until the odour from the chlorine compounds formed disappears (see note 4). Cool rapidly to room temperature.

NOTES

1 The dissolution procedures (7.3.1) may be incomplete for particular samples (for example samples with high contents of chromium and carbon). In such cases a fusion of the residue is required, and the result of this fusion shall be added to the test solution.

2 The violet colour of the permanganic acid will be observed. If the test portion contains only a very small amount of manganese, add about 5 ml of manganese sulfate solution (4.13), so that the permanganic acid is visible.

3 The addition of hydrochloric acid (4.7) must be made after complete oxidation, visible by the violet colour-formation of the permanganic acid.

4 In the case of a visual titration (7.3.3.2), after the decomposition of the permanganic acid and after boiling for 10 min, it is necessary to add 4 ml of manganese sulfate solution (4.14), then boil for a further 3 min.

7.3.3 Titration**7.3.3.1 Potentiometric titration****7.3.3.1.1 In the absence of vanadium**

Place the electrodes of the potentiometric device (5.1) into the beaker containing the solution (7.3.2) to be titrated.

Agitate, preferably with an electromagnetic stirrer, and add from a burette the ammonium iron(II) sulfate standard solution (4.19) until a potential drop occurs (see the note). Titrate slowly around this point. Let V_4 be this volume in millilitres.

With the platinum-saturated calomel electrodes the potential drop is of the order of 300 mV and the equivalence point occurs between 700 and 900 mV.

NOTE — With chromium contents in solution less than 40 mg, use a 20 ml burette, and with chromium contents in solution more than 40 mg, use a 50 ml burette.

7.3.3.1.2 In the presence of vanadium

Titrate as indicated in 7.3.3.1.1. In this case the vanadium is measured along with the chromium. Let V_5 be this volume in millilitres. The vanadium titrated with the chromium is oxidized by potassium permanganate solution (4.15). To oxidize the

vanadium alone, measure the oxidation potential with the platinum-saturated calomel electrodes while potassium permanganate solution (4.15) is being added. Add potassium permanganate solution (4.15) drop by drop until a potential of 1 000 to 1 160 mV is obtained.

Maintain this potential for 2 min, after which, either

— eliminate the excess potassium permanganate by the addition of about 10 ml of sodium nitrite solution (4.16); about a minute later add 3 g of urea (4.1); wait for the potential to become stabilized at around 800 mV, agitate and titrate as indicated in 7.3.3.1.1; or

— eliminate the excess potassium permanganate by the addition, drop by drop, of sodium nitrite solution (4.16) until the potential stabilizes at around 770 mV; add 5 ml of sulfamic acid solution (4.17) (potential 780 mV); then add 30 ml of orthophosphoric acid (4.4), agitate and titrate as indicated in 7.3.3.1.1.

Let V_6 be this volume in millilitres.

7.3.3.2 Visual titration (see the note).

Whilst stirring, add from a burette accurately known amounts of the ammonium iron(II) sulfate standard solution (4.19) until the colour of the solution changes from orange-yellow to bluish-green. Add 5 ml of the ammonium iron(II) sulfate standard solution (4.19) in excess and continue to stir for 5 s.

Let V_7 be this volume in millilitres.

Titrate immediately the excess ammonium iron(II) sulfate with the potassium permanganate standard solution (4.18). Take as the end point of titration, the beginning of the slight permanent darkening of the pale green colour, which is very clear and well-defined to an experienced operator.

Let V_8 be this volume in millilitres.

Add a further 2 drops of the potassium permanganate standard solution (4.18). The violet shade due to excess potassium permanganate shall persist for at least 5 min.

NOTE — Apply the visual titration technique only to test portions containing less than 3 mg of vanadium.

8 Expression of results**8.1 Method of calculation****8.1.1 Potentiometric titration****8.1.1.1 In the absence of vanadium.**

The percentage by mass of chromium (Cr) is given by the expression

$$\frac{(V_4 - V_0) \times c_1}{m \times 1\,000} \times 100 = \frac{(V_4 - V_0) \times c_1}{m \times 10}$$

where

V_0 is the volume, in millilitres, of the ammonium iron(II) sulfate standard solution (4.19) used for titrating the blank test (7.2);

V_4 is the volume, in millilitres, of the ammonium iron(II) sulfate standard solution (4.19) used for titrating the chromium (7.3.3.1.1);

c_1 is the corresponding concentration of the ammonium iron(II) sulfate standard solution (4.19), expressed as milligrams of chromium per millilitre;

m is the mass, in grams, of the test portion.

8.1.1.2 In the presence of vanadium

The percentage by mass of chromium (Cr) is given by the expression

$$\frac{(V_5 - V_6) \times c_1}{m \times 1000} \times 100 = \frac{(V_5 - V_6) \times c_1}{m \times 10}$$

where

V_5 is the volume, in millilitres, of the ammonium iron(II) sulfate standard solution (4.19) used for titrating the chromium and the vanadium;

V_6 is the volume, in millilitres, of the ammonium iron(II) sulfate standard solution (4.19) used for titrating the vanadium;

c_1 is the corresponding concentration of the ammonium iron(II) sulfate standard solution (4.19), expressed as milligrams of chromium per millilitre;

m is the mass, in grams, of the test portion.

8.1.2 Visual titration

The percentage by mass of chromium (Cr) is given by the expression

$$\begin{aligned} & [(V_7 \times c'_1) - (V_8 \times c_2)] \times \frac{100}{m \times 1000} \\ &= \frac{(V_7 \times c'_1) - (V_8 \times c_2)}{m \times 10} \end{aligned}$$

where

V_7 is the volume, in millilitres, of the ammonium iron(II) sulfate standard solution (4.19) added to reduce the chromium;

V_8 is the volume, in millilitres, of the potassium permanganate standard solution (4.18) used for the back titration;

c'_1 is the corresponding concentration of the ammonium iron(II) sulfate standard solution (4.19), expressed as milligrams of chromium per millilitre;

c_2 is the corresponding concentration of the potassium permanganate standard solution (4.18), expressed as milligrams of chromium per millilitre;

m is the mass, in grams, of the test portion.

8.2 Precision

A planned trial of this method was carried out by eleven laboratories at ten levels of chromium, each laboratory making two determinations at each level.

The test samples used are detailed in annex A.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between chromium content, repeatability (r) and reproducibility (R) of the test results as summarized in table 1 (potentiometric titration) and table 2 (visual titration).

The graphical presentation of the relationships is given in annex B.

Table 1 — Potentiometric titration

Level of chromium % (m/m)	Repeatability r	Reproducibility R
0,250	0,013	0,019
0,500	0,019	0,028
1,00	0,027	0,041
2,5	0,044	0,067
5,0	0,064	0,098
10,0	0,092	0,143
15,0	0,114	0,179
20,0	0,132	0,209
25,0	0,149	0,236
35,0	0,178	0,284

Table 2 — Visual titration

Level of chromium % (m/m)	Repeatability r	Reproducibility R
0,250	0,017	0,030
0,500	0,025	0,044
1,00	0,038	0,065
2,5	0,063	0,108
5,0	0,093	0,159
10,0	0,138	0,234
15,0	0,174	0,294
20,0	0,205	0,345
25,0	0,233	0,391
35,0	0,281	0,471

9 Test report

The test report shall include the following information:

- the method used, by reference to this International Standard;
- the results, and the form in which they are expressed;
- any unusual features noted during the determination;
- any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Annex A

Additional information on the international co-operative tests

(This annex does not form an integral part of the Standard.)

Tables 1 and 2 in sub-clause 8.2 have been derived from the results of the international analytical trials carried out in 1983-1984 on ten steel and iron samples in four countries involving eleven laboratories.

The results of the trials were given in reports issued by ISO TC 17/SC 1 in 1984 (documents N 578, N 588 and N 599).

The test samples used had the compositions shown in table 3.

Table 3 — Composition of test samples

Sample	Chemical composition % (m/m)								
	Cr	C	Si	Mn	Mo	Ni	V	W	Co
IRSID 102-1	0,261	0,389	0,281	0,367	1,2	4,4	—	—	—
BAM 182-1	0,591	0,790	0,368	0,389	—	0,152	0,177	—	—
IRSID 110-1	1,54	0,987	0,446	0,367	—	0,378	0,259	—	—
IRSID 210-1	3,92	0,762	0,200	0,250	8,15	—	1,650	1,54	0,185
IRSID 276-1	5,29	0,364	0,985	0,368	1,47	0,178	0,541	—	—
IRSID 201-1	12,33	0,291	0,843	0,363	—	0,202	(0,02)	—	—
IRSID 279-2	15,64	0,088	0,516	0,258	—	1,603	(0,02)	—	—
CTIF A	(19,5)	(2,5)	(0,45)	(0,655)	(1,4)	(1,2)	(0,02)	—	—
IRSID B	(27,0)	(0,02)	(0,27)	(0,115)	(0,016)	(0,15)	(0,014)	—	(0,32)
NBS 890	32,4	2,91	0,67	0,62	0,018	0,397	0,45	—	—

() not certified value.

NOTES

1 The statistical analysis has been performed in accordance with ISO 5725.

2 Ten samples were used for the co-operative tests. However, as the visual titration is applicable only to samples containing less than 3 mg of vanadium in the test portion, only six points have been illustrated on figure 2 in annex B (the data for samples 182-1, 110-1, 276-1 and 210-1 having been omitted).

Annex B

Graphical representation of precision data

(This annex does not form an integral part of the Standard.)

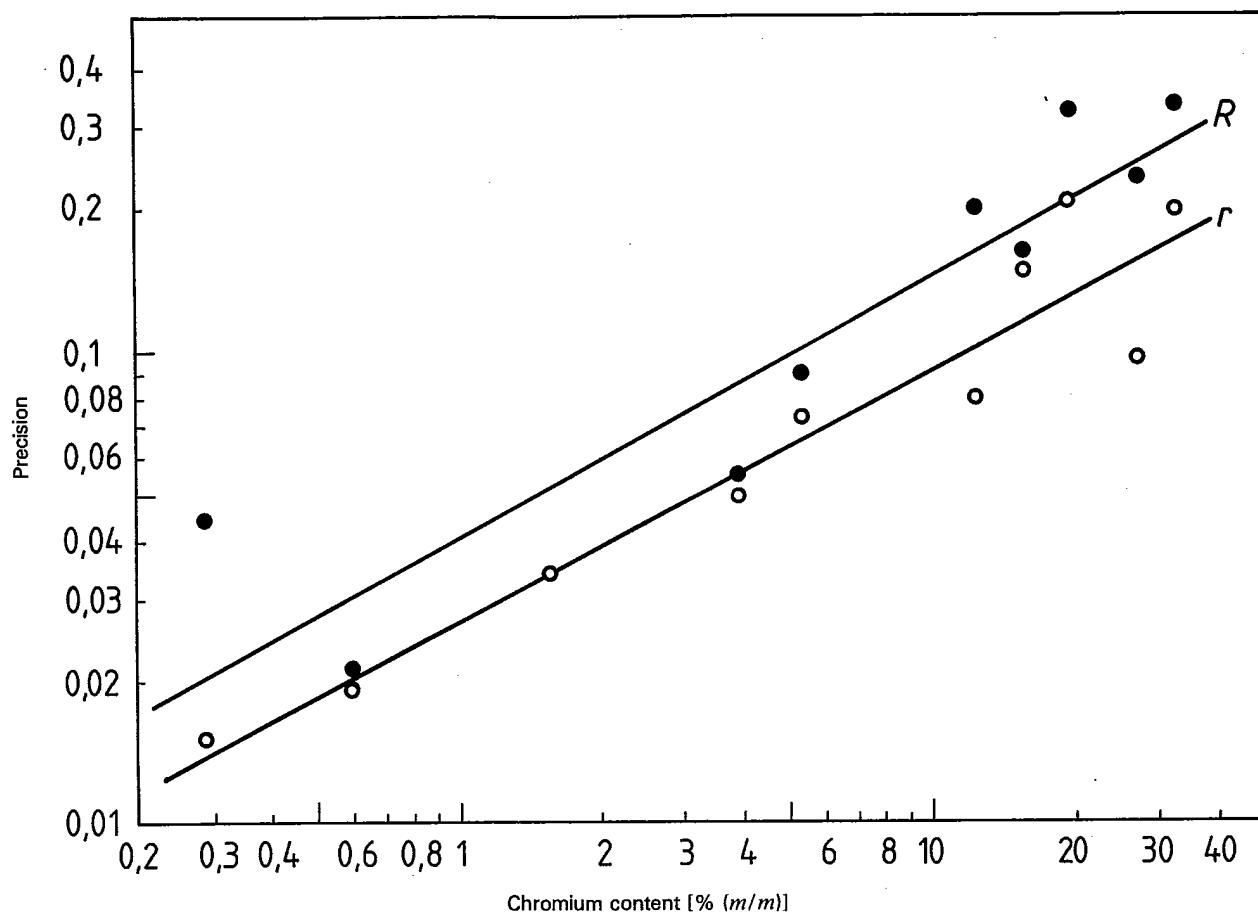


Figure 1 — Potentiometric titration — Logarithmic relationship between chromium content and repeatability (r) and reproducibility (R)

ISO 4937-1986 (E)

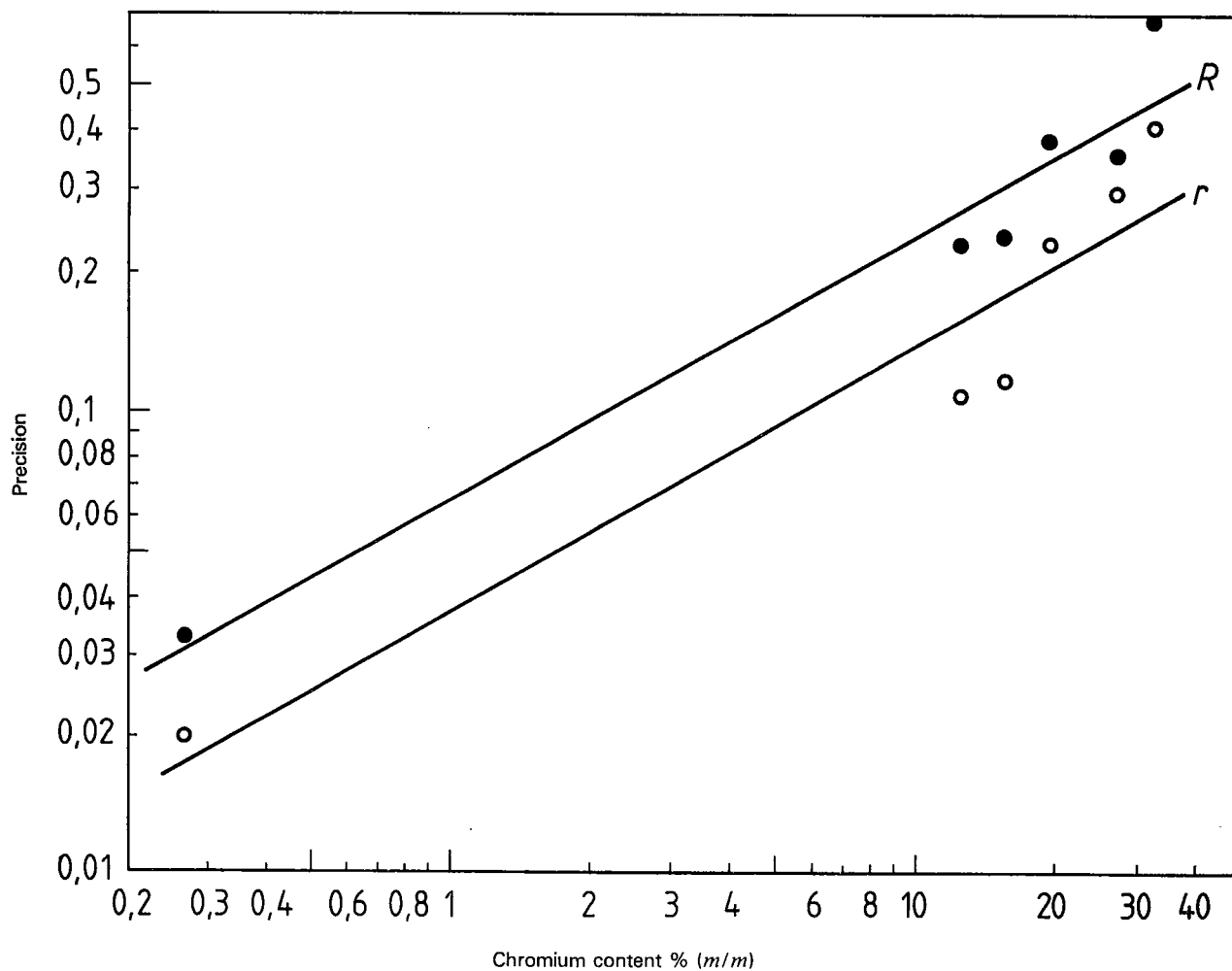


Figure 2 — Visual titration — Logarithmic relationship between chromium content and repeatability (r) and reproducibility (R)