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ISO 591-1

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Titanium dioxide pigments for paints —

Part 1:
Specifications and methods of test

Pigments de dioxyde de titane pour peintures —

Partie 1: Spécifications et méthodes d'essai

Reference number
ISO 591-1:2000(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 part of ISO 591 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 591-1 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 2, *Pigments and extenders*.

This part of ISO 591 cancels and replaces ISO 591:1977, which has been technically revised. In contrast to ISO 591:1977, which specified the Nakazono reductor method for the determination of the titanium dioxide content and allowed other methods to be used by agreement between the interested parties, ISO 591-1 contains two methods (see clause 7).

ISO 591 consists of the following parts, under the general title *Titanium dioxide pigments for paints*:

- *Part 1: Specifications and methods of test*
- *Part 2: Determination of the content of secondary constituents*

Titanium dioxide pigments for paints —

Part 1:
Specifications and methods of test

1 Scope

This part of ISO 591 specifies the requirements and corresponding methods of test for titanium dioxide pigments for paints.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 591. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 591 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.

ISO 787-1:1982, *General methods of test for pigments and extenders — Part 1: Comparison of colour of pigments*.

ISO 787-2:1981, *General methods of test for pigments and extenders — Part 2: Determination of matter volatile at 105 °C.*

ISO 787-3:2000, *General methods of test for pigments and extenders — Part 3: Determination of matter soluble in water — Hot extraction method*.

ISO 787-5:1980, *General methods of test for pigments and extenders — Part 5: Determination of oil absorption value*.

ISO 787-9:1981, *General methods of test for pigments and extenders — Part 9: Determination of pH value of an aqueous suspension*.

ISO 787-14:1973, *General methods of test for pigments — Part 14: Determination of resistivity of aqueous extract*.

ISO 787-18:1983, *General methods of test for pigments and extenders — Part 18: Determination of residue on sieve — Mechanical flushing procedure*.

ISO 787-24:1985, *General methods of test for pigments and extenders — Part 24: Determination of relative tinting strength of coloured pigments and relative scattering power of white pigments — Photometric methods*.

ISO 787-25:1993, *General methods of test for pigments and extenders — Part 25: Comparison of the colour, in full-shade systems, of white, black and coloured pigments – Colorimetric method*.

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 15528:2000, *Paints, varnishes and raw materials for paints and varnishes — Sampling*.

3 Term and definition

For the purposes of this part of ISO 591, the following term and definition apply.

3.1
titanium dioxide pigment
pigment consisting essentially of titanium dioxide (TiO_2) of the anatase or the rutile crystal structure, as determined by X-ray examination

4 Classification

4.1 Types

This part of ISO 591 covers two types of titanium dioxide pigment, as follows:

Type A: Anatase type

Type R: Rutile type

4.2 Grades

The pigments are further classified into the following grades:

Grade A1	Type A
Grade A2	
Grade R1	Type R
Grade R2	
Grade R3	

5 Required characteristics and associated tolerances

5.1 Appearance

The material shall be in the form of a soft, dry powder or in such a condition that it may be readily reduced thereto by crushing under a palette knife, without any grinding action.

5.2 Other characteristics

5.2.1 For titanium dioxide pigments complying with this part of ISO 591, the essential requirements are specified in Table 1 and the conditional requirements are listed in Table 2. The conditional requirements shall be specified by agreement between the interested parties.

The requirement for matter volatile at 105 °C after preconditioning in Table 2 shall only apply if this characteristic is explicitly specified by the interested parties or in a contract.

5.2.2 The agreed reference pigment referred to in Table 2 shall comply with the requirements of Table 1.

Table 1 — Essential requirements

Characteristic	Requirement depending on type and grade					Method of test
	Type A		Type R			
	A1	A2	R1	R2	R3	
Titanium dioxide content % (by mass), min.	98	92	97	90	80	See clause 7
Matter volatile at 105 °C at point of acceptance % (by mass), max.	0,5	0,8	0,5	To be agreed between the interested parties		ISO 787-2
Matter soluble in water % (by mass), max.	0,6	0,5	0,6	0,5	0,7	ISO 787-3[a]
Residue on sieve (45 µm) % (by mass), max.	0,1	0,1	0,1	0,1	0,1	ISO 787-18 or other agreed method

[a] If necessary, a coagulation agent may be used.

Table 2 — Conditional requirements

Characteristic	Requirement depending on type and grade					Method of test
	Type A		Type R			
	A1	A2	R1	R2	R3	
Colour	Similar to that of the agreed reference pigment (see 5.2.2)					ISO 787-1 or ISO 787-25[a]
Scattering power	To be agreed between the interested parties					ISO 787-24
Matter volatile at 105 °C after 24 h preconditioning at (23 ± 2) °C and (50 ± 5) % relative humidity % (by mass), max.[b]	0,5	0,8	0,5	1,5	2,5	ISO 787-2
pH of aqueous suspension	Similar to that of the agreed reference pigment (see 5.2.2)					ISO 787-9
Oil absorption value						ISO 787-5
Resistivity of aqueous extract	—	Similar to that of the agreed reference pigment (see 5.2.2)	—	Similar to that of the agreed reference pigment (see 5.2.2)		ISO 787-14

[a] By agreement only.

[b] See 5.2.1.

6 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528.

7 Determination of titanium dioxide content

7.1 General

For the determination of the titanium dioxide content, two methods (A and B) are provided. In cases of dispute, either of the methods may be used as the referee method, by agreement between the interested parties.

Method A uses aluminium metal as the reducing agent. It is suitable for individual determinations and for routine analysis.

Method B uses chromium(II) chloride and zinc amalgam as reducing agents and can be automated. It is particularly suitable as a routine method.

7.2 Method A: Aluminium reduction method

7.2.1 Principle

A test portion of the dried sample is dissolved in sulfuric acid, with the addition of ammonium sulfate. The titanium(IV) is then reduced to titanium(III) with aluminium under a carbon dioxide atmosphere. The solution is then titrated with ammonium iron(III) sulfate, using ammonium thiocyanate as indicator.

7.2.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity as defined in ISO 3696.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

7.2.2.1 Hydrochloric acid, concentrated, approximately 37 % (by mass), $\rho \approx 1{,}19$ g/ml.

7.2.2.2 Sulfuric acid, concentrated, approximately 96 % (by mass), $\rho \approx 1{,}84$ g/ml.

7.2.2.3 Ammonium sulfate.

7.2.2.4 Sodium hydrogen carbonate, saturated solution.

Prepare this solution at the time of use. About 10 g of sodium hydrogen carbonate ($NaHCO_3$) to 90 ml of water are required.

7.2.2.5 Ammonium thiocyanate indicator.

Dissolve 24,5 g of ammonium thiocyanate (NH_4SCN) in 80 ml of hot water, filter, cool to room temperature and dilute to 100 ml. Keep in a well-stoppered, dark-coloured bottle.

7.2.2.6 Ammonium iron(III) sulfate, standard volumetric solution, 1 ml equivalent to 0,004 8 g of TiO_2.

7.2.2.6.1 Preparation

Dissolve, in a 1 000 ml one-mark volumetric flask, 30 g of freshly prepared ammonium iron(III) sulfate [$(FeNH_4(SO_4)_2 \cdot 12H_2O$] in 300 ml of water containing 15 ml of sulfuric acid (7.2.2.2). Add potassium permanganate solution (7.2.2.7), drop by drop, until the solution is pink coloured. Dilute to the mark with water and mix well. Filter if the solution is cloudy.

7.2.2.6.2 Standardization

Standardize the solution using 190 mg to 210 mg of titanium dioxide reference standard, dried to constant mass at (105 ± 2) °C, following the procedure described in 7.2.4.3.

Calculate the titanium dioxide equivalent T_1 of the solution, expressed in grams of TiO_2 per millilitre, using the equation

$$T_1 = \frac{m_1 \times P}{V_1 \times 100}$$

where

m_1 is the mass, in grams, of reference standard used;

P is the titanium dioxide content of the reference standard, expressed as a percentage by mass (i.e. 99,74 %);

V_1 is the volume, in millilitres, of the ammonium iron(III) sulfate solution required in the titration.

7.2.2.7 **Potassium permanganate,** standard volumetric solution, $c(\frac{1}{5}KMnO_4)$ = 0,1 mol/l.

Dissolve 3,160 7 g of potassium permanganate in 500 ml of water in a 1000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

7.2.2.8 **Aluminium metal,** electrolytic grade, for example in the form of foil, sheet or cut wire.

7.2.3 Apparatus

Use ordinary laboratory apparatus and burettes, pipettes and one-mark volumetric flasks complying with the requirements of ISO 385-1, ISO 648 and ISO 1042, respectively, together with the following:

7.2.3.1 **Delivery tube:** an essentially U-shaped glass tube, 4 mm in internal diameter, comprising a horizontal section and two vertical arms, one of the vertical arms being 150 mm long and the other 75 mm long.

As an alternative, an absorption apparatus as shown in Figure 1 or a Contat-Göckel cap as shown in Figure 2 may be used.

7.2.3.2 **Weighing bottle,** wide-mouth, with an external-fitting cap, and no larger than necessary for the test portion.

7.2.3.3 **Oven,** capable of maintaining a temperature of (105 ± 2) °C.

7.2.3.4 **Desiccator,** containing a suitable desiccant, for example silica gel.

7.2.4 Procedure

7.2.4.1 General

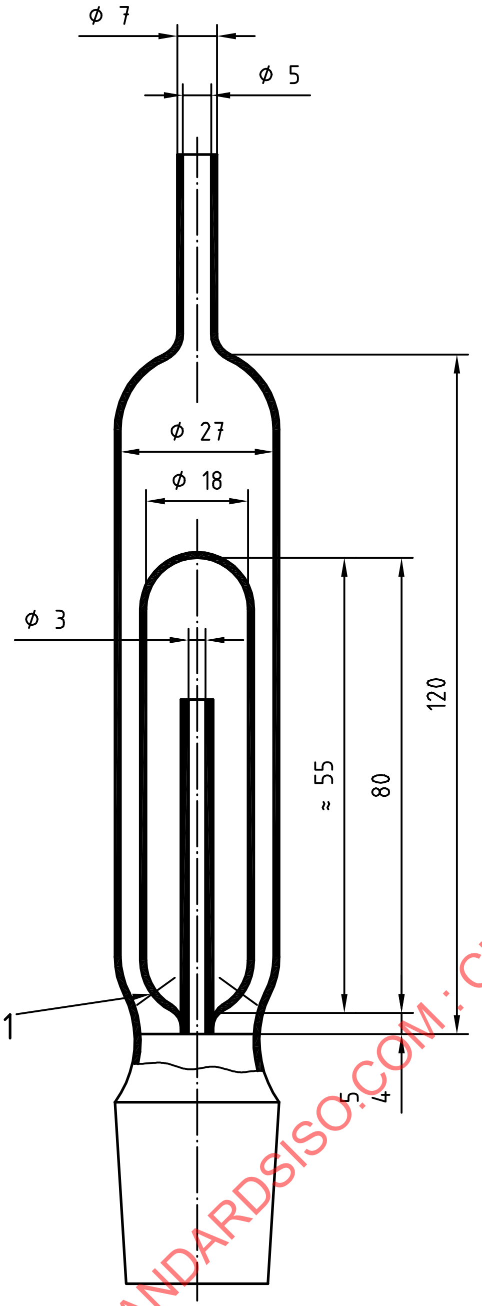
Carry out the determination in duplicate.

7.2.4.2 Test portion

Take about 10 g of the sample (see clause 6) and dry it in the open weighing bottle (7.2.3.2) at (105 ± 2) °C to constant mass. Cap the bottle and allow it to cool to room temperature in the desiccator (7.2.3.4).

Weigh out, to the nearest 0,1 mg, 190 mg to 210 mg of this test sample (m_2).

Dimensions in millimetres



Key

1 Four openings (∅ 1 mm to 2 mm)

Figure 1 — Possible absorption apparatus

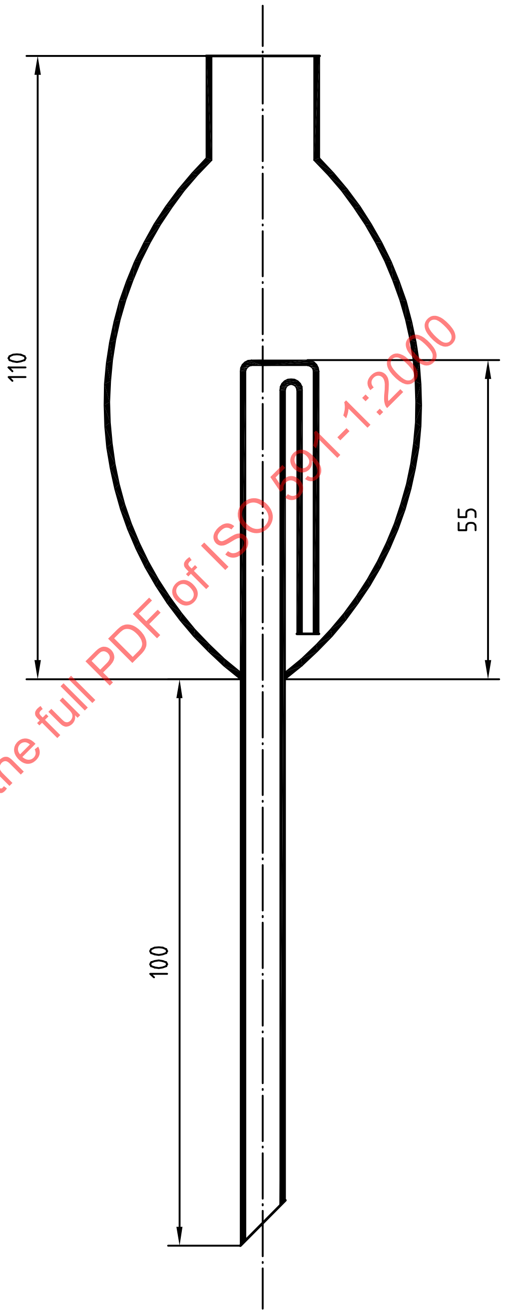


Figure 2 — Possible absorption apparatus (Contat-Göckel cap)

7.2.4.3 Determination

Transfer the test portion to a dry, wide-necked 500 ml conical flask. Add 7 g to 8 g of ammonium sulfate (7.2.2.3) and 20 ml of sulfuric acid (7.2.2.2). Mix well and heat on a hotplate until dense white fumes are evolved. Continue heating strongly until dissolution is complete (usually requires max. 5 min of boiling) or until it is apparent that the residue is composed of SiO_2 or siliceous matter. Cool and, with caution, add 120 ml of water and 20 ml of hydrochloric acid (7.2.2.1). Bring to the boil again and then remove from the heat.

Insert the short arm of the delivery tube (7.2.3.1) into a hole in a rubber stopper which fits the conical flask, or use an absorption apparatus. Place approximately 1 g of aluminium metal (7.2.2.8) in the flask. Ensure that the end of the long arm of the delivery tube is near the bottom of a 250 ml beaker containing about 150 ml of sodium hydrogen carbonate solution (7.2.2.4), or place the solution in the absorption apparatus.

As soon as the dissolution of the aluminium is complete, heat the contents of the flask to gentle boiling for 3 min to 5 min without removing the delivery tube from the sodium hydrogen carbonate solution. Cool to about 60 °C, preferably by partial immersion of the flask in a vessel of water. The sodium hydrogen carbonate solution should siphon into the flask during this cooling, giving an atmosphere of carbon dioxide over the reduced titanium solution. Withdraw the stopper, and rinse the stopper and the delivery tube with a little water, collecting the rinse water in the flask before removing the stopper and delivery tube completely.

Add 2 ml of ammonium thiocyanate indicator solution (7.2.2.5) and titrate immediately with ammonium iron(III) sulfate solution (7.2.2.6) to a pink-coloured endpoint. It is best to add the bulk of the ammonium iron(III) sulfate solution at once, shake well, and finish the titration drop by drop. Record the volume of ammonium iron(III) sulfate solution used (V_2).

7.2.5 Expression of results

7.2.5.1 Calculation

Calculate the titanium dioxide content $w(\mathrm{TiO_2})$, expressed as a percentage by mass, using the equation

$$w(\mathrm{TiO_2}) = \frac{V_2 \times T_1 \times 100}{m_2}$$

where

m_2 is the mass, in grams, of the test portion, dried to constant mass;

V_2 is the volume, in millilitres, of the ammonium iron(III) sulfate solution (7.2.2.6) used in the determination;

T_1 is the titanium dioxide equivalent, in grams per millilitre, of the ammonium iron(III) sulfate solution (see 7.2.2.6.2).

Calculate the mean of the two determinations and report the result to the nearest 0,1 % (by mass).

NOTE The calculated results include chromium, arsenic and any other substance that is reduced by aluminium and subsequently oxidized by iron(III). However, appreciable quantities of interfering materials are not likely to be encountered in the titanium dioxide pigments usually used in paints and related products.

7.2.5.2 Precision

No precision data are currently available.

7.3 Method B: Chromium(II) chloride reduction method

7.3.1 Principle

A test portion of the dried sample is heated with molten potassium pyrosulfate, and the melt is dissolved in hydrochloric acid. The titanium(IV) is then reduced to titanium(III) with chromium(II) chloride solution under a carbon dioxide atmosphere. The solution is then titrated with potassium dichromate, using potentiometric indication of the endpoint.

7.3.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity as defined in ISO 3696.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

7.3.2.1 **Hydrochloric acid,** concentrated, approximately 37 % (by mass), $\rho \approx 1{,}19$ g/ml.

7.3.2.2 **Sulfuric acid,** concentrated, approximately 96 % (by mass), $\rho \approx 1{,}84$ g/ml.

7.3.2.3 **Sulfuric acid,** dilute, approximately 5 % (by mass).

7.3.2.4 **Potassium pyrosulfate** ($K_2S_2O_7$), fine powder.

7.3.2.5 **Chromium(III) chloride**[1]**,** solution, $c(CrCl_3{\cdot}6H_2O) = 0{,}3$ mol/l.

Dissolve, in a 1 000 ml one-mark volumetric flask, 79,93 g of chromium(III) chloride hexahydrate, $CrCl_3{\cdot}6H_2O$, in 300 ml of water containing 100 ml of hydrochloric acid (7.3.2.1). Dilute to the mark with water and mix well.

7.3.2.6 **Chromium(II) chloride,** solution, $c(CrCl_2) = 0{,}3$ mol/l, prepared by reduction of chromium(III) chloride with zinc amalgam, as follows:

$$2Cr^{3+} + 2e^- \rightarrow 2Cr^{2+} \qquad (E_0 = -0{,}41\ V)$$

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad (E_0 = +0{,}76\ V)$$

$$2Cr^{3+} + Zn \rightarrow 2Cr^{2+} + Zn^{2+} \qquad (E_0 = +0{,}35\ V)$$

7.3.2.6.1 **Precautions**

7.3.2.6.1.1 As zinc amalgam is stored in dilute sulfuric acid, it is very important to separate the amalgam from the solution to avoid dilution of the chromium(II) chloride solution to be prepared. Transfer the zinc amalgam as described in 7.3.2.6.2.1.

7.3.2.6.1.2 Store the chromium(II) chloride solution obtained in a brown glass bottle under petroleum ether to minimize oxidation. Ensure that all precautions are taken to preserve the solution from oxidation by always operating in an inert atmosphere (carbon dioxide).

Chromium(II) chloride solutions are unstable. Prepare a fresh solution each day.

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[1] Information on suppliers of chromium(III) chloride can be obtained through the Secretariat of ISO/TC 35/SC 2, c/o DIN Deutsches Institut für Normung e.V., Burggrafenstraße 6, D-10787 Berlin.

7.3.2.6.2 Preparation

7.3.2.6.2.1 Transfer of zinc amalgam to the reductor

Transfer the zinc amalgam (7.3.2.8) to a separator (Nakazono reductor or separating funnel). Separate the amalgam at the base of the separator from the sulfuric acid (in beaker 1 amalgam only, in beaker 2 sulfuric acid). Transfer the amalgam in beaker 1 to the reductor.

7.3.2.6.2.2 Reduction of chromium(III) to chromium(II)

Pour approximately 200 ml of chromium(III) chloride solution (7.3.2.5) into a beaker. Heat the solution to 60 °C. Pour the hot solution into the reductor. Flush with carbon dioxide for 3 min. Close the stopcock connecting the reduction vessel with the atmosphere, then close the stopcock supplying carbon dioxide to the reductor so that the contents of the apparatus remain under an inert atmosphere. Shake the solution for 5 min (the colour of the solution, green at the beginning, changes to intense blue when reduced).

7.3.2.6.2.3 Transfer to the titration flask

Transfer the solution to a brown glass titration flask containing petroleum ether, using the following procedure. Pass carbon dioxide into the reductor by opening the upper stopcock and leaving it open during the following operations. Attach one end of a length of tubing to the base of the reductor. Open the lower stopcock of the reductor and recover the amalgam in a vessel containing dilute sulfuric acid (7.3.2.3). Then, with the other end of the tubing under the petroleum ether layer, transfer the solution to the titration flask.

7.3.2.7 Potassium dichromate, standard volumetric solution, $c(\frac{1}{6}\,K_2Cr_2O_7) = 0{,}06$ mol/l, 1 ml equivalent to 0,004 8 g of TiO_2.

7.3.2.7.1 Preparation

Dry a sufficient quantity of $K_2Cr_2O_7$ in an oven at (105 ± 2) °C to constant mass. Allow to cool in a desiccator. Weigh out 2,941 8 g of the dried potassium dichromate to the nearest 0,1 mg. Transfer to a 1 000 ml one-mark volumetric flask, dissolve in water, dilute to the mark with water and mix well.

7.3.2.7.2 Standardization

Standardize the solution using the titanium dioxide reference standard, dried to constant mass at (105 ± 2) °C, following the procedure described in 7.3.4.3. Prepare four separate solutions and calculate the titanium dioxide equivalent T_2 of the solution, expressed in grams of TiO_2 per millilitre, using the following equation:

$$T_2 = \frac{m_1 \times P}{(V_2 - V_1) \times 100}$$

where

m_1 is the mass, in grams, of reference standard used;

P is the titanium dioxide content of the reference standard, expressed as a percentage by mass (i.e. 99,74 %);

V_1 is the volume, in millilitres, of potassium dichromate solution (7.3.2.7) required to oxidize the excess chromium(II) chloride;

V_2 is the volume, in millilitres, of potassium dichromate solution (7.3.2.7) required to oxidize the excess chromium(II) chloride plus the reduced titanium.

7.3.2.8 **Zinc amalgam,** 3 % (by mass).

WARNING — Mercury is toxic. Avoid skin contact and inhalation of vapour. Carry out all procedures in a well-ventilated fume cupboard.

Place 50 ml of mercury in a porcelain dish on a steam bath in a fume cupboard. Cover the surface of the mercury with dilute sulfuric acid (7.3.2.3). Add 20 g to 30 g of zinc in small granules. Stir from time to time and replenish the dilute acid with water as required. When all the solid zinc has disappeared, allow the amalgam to cool and stand for several hours. Finally, filter through a Gooch crucible with no filter pad. Keep the amalgam in a small bottle under dilute sulfuric acid (7.3.2.3).

7.3.2.9 **Carbon dioxide,** in a steel cylinder.

7.3.3 Apparatus

Use ordinary laboratory apparatus and burettes, pipettes and one-mark volumetric flasks complying with the requirements of ISO 385-1, ISO 648 or ISO 1042, respectively, together with the following:

7.3.3.1 **Nakazono reductor** or **separating funnel.**

7.3.3.2 **Weighing bottle,** wide-mouth, with an external-fitting cap, and no larger than necessary for the test portion.

7.3.3.3 **Oven,** capable of maintaining a temperature of (105 ± 2) °C.

7.3.3.4 **Desiccator,** containing a suitable desiccant, for example silica gel.

7.3.3.5 **Silica flask,** capacity 250 ml.

7.3.3.6 **Meker burner,** burning a gas/oxygen mixture.

7.3.3.7 **Automatic titrator,** with a microprocessor for endpoint determination.

7.3.3.8 **Gold-wire indicator electrode.**

7.3.3.9 **Calomel reference electrode.**

7.3.3.10 **Hotplate,** capable of being maintained at a constant temperature of 60 °C.

7.3.3.11 **Stirrer.**

7.3.4 Procedure

7.3.4.1 General

Carry out the determination in duplicate.

7.3.4.2 Test portion

Take about 10 g of the sample (see clause 6) and dry it in the open weighing bottle (7.3.3.2) at (105 ± 2) °C to constant mass. Cap the bottle and allow it to cool to room temperature in the desiccator.

Weigh out, to the nearest 0,1 mg, 0,5 g of this test sample (m_3).

7.3.4.3 Determination

Fuse (25 ± 1) g of potassium pyrosulfate (7.3.2.4) in the silica flask (7.3.3.5) and continue to heat until fuming ceases. Allow to cool.