SLOVENSKI STANDARD

SIST EN 196-2
prva izdaja
september 1995

Metode preskušanja cementa - 2. del: Kemijska analiza cementa (prevzet standard EN 196-2:1994 z metodo platnice)

Methods of testing cement - Part 2: Chemical analysis of cement

Méthodes d'essais des ciments - Partie 2: Analyse chimique des ciments

Prüfverfahren für Zement - Teil 2: Chemische Analyse von Zement

Deskriptorji: cement, kemijska analiza, določanje sestavin, žarna izguba, sulfat, sulfid, mangan, silicijev dioksid, železov oksid, aluminijev oksid, kalcijev oksid, magnezijev oksid, ostanek po odkajanju, gravimetrično določanje, spektrofotometrični postopek, EDTO

Referenčna številka
SIST EN 196-2:1995 (en)

ICS 91.100.10

Nadaljevanje na straneh od II do IV in 1 do 21

UVOD

Standard SIST EN 196-2 (en), Metode preskušanja cementa - 2. del: Kemijska analiza cementa, prva izdaja, 1995, ima status slovenskega standarda in je z metodo platnice prevzet evropski standard EN 196-2, Methods of testing cement - Part 2: Chemical analysis of cement, 1994, v angleškem jeziku.

NACIONALNI PREDGOVOR

Evropski standard EN 196-2:1994 je pripravil tehnični odbor Evropske organizacije za standardizacijo CEN/TC 51 Cement in apno.

Odločitev za prevzem tega standarda po metodi platnice je sprejela delovna skupina USM/TC CAA/WG 1 Cement, potrdil pa tehnični odbor USM/TC CAA Cement, apno in vlaknatocementni izdelki.

Ta slovenski standard je dne 1995-08-29 odobril direktor USM.

SLOVENSKI STANDARD SIST EN 196 ZA PRESKUŠANJE CEMENTA OBSEGA NASLEDNJE DELE:

SIST EN 196-1:1995 (en)	Metode preskušanja cementa - 1. del: Določanje trdnosti
SIST EN 196-2:1995 (en)	Metode preskušanja cementa - 2. del: Kemijska analiza cementa
SIST EN 196-3:1995 (en)	Metode preskušanja cementa - 3. del: Določanje časa vezanja in prostorninske obstojnosti
SIST ENV 196-4:1995 (en)	Metode preskušanja cementa - 4. del: Kvantitativno določanje sestavin
SIST EN 196-5:1995 (en)	Metode preskušanja cementa - 5. del: Določanje pucolanske aktivnosti za pucolanske cemente
SIST EN 196-6:1995 (en)	Metode preskušanja cementa - 6. del: Določanje finosti
SIST EN 196-7:1995 (en)	Metode preskušanja cementa - 7. del: Metode odvzemanja in priprave vzorcev cementa
SIST EN 196-21:1995 (en)	Metode preskušanja cementa - 21. del: Določanje količine kloridov, ogljikovega dioksida in alkalij v cementu

PREDHODNA IZDAJA

- JUS B.C8.020:1975 (sh)	Cementi - Metode hemijskog ispitivanja cemenata proizvedenih na bazi portland klinkera

OSNOVA ZA IZDAJO STANDARDA

- Prevzem standarda EN 196-2:1994

OPOMBI

- Povsod, kjer se v besedilu standarda uporablja izraz "evropski standard", v SIST EN 196-2:1995 to pomeni "slovenski standard".
- Uvod in nacionalni predgovor nista sestavni del standarda.

VSEBINA

Po mnenju Ministrstva za informiranje Republike Slovenije z dne 18. februarja 1992, štev. 23/96-92, spada ta publikacija med proizvode informativne narave iz 13. točke tarifne številke 3, za katere se plačuje 5-odstotni prometni davek.

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 196-2

December 1994

ICS 91.100.10

Supersedes EN 196-2:1987

Descriptors: Cement, chemical analysis, determination of content, losses on ignition, sulphates, sulphides, manganese, silicon dioxide, iron oxides, aluminium oxides, calcium oxides, magnesium oxides, evaporation residue, gravimetric analysis, spectrophotometric analysis, EDTA

English version

Methods of testing cement - Part 2: Chemical analysis of cement

Méthodes d'essais des ciments - Partie 2: Analyse chimique des ciments

Prüfverfahren für Zement - Teil 2: Chemische Analyse von Zement

This European Standard was approved by CEN on 1994-12-12. CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

The European Standards exist in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart,36 B-1050 Brussels

Ref. No. EN 196-2:1994 E

Contents

Foreword

This European Standard was drawn up by CEN/TC 51 'Cement and building limes' the secretariat of which is held by IBN.

The standard on the methods of testing cement comprises the following Parts:

EN 196-1	Methods of testing cement — Part 1: Determination of strength
EN 196-2	Methods of testing cement — Part 2: Chemical analysis of cement
EN 196-3	Methods of testing cement — Part 3: Determination of setting time and soundness
ENV 196-4	Methods of testing cement — Part 4: Quantitative determination of constituents
EN 196-5	Methods of testing cement — Part 5: Pozzolanicity test for pozzolanic cements
EN 196-6	Methods of testing cement — Part 6: Determination of fineness
EN 196-7	Methods of testing cement — Part 7: Methods of taking and preparing samples of cement
EN 196-21	Methods of testing cement — Part 21: Determination of the chloride, carbon dioxide and alkali content of cement

This European Standard shall be given the status of a National Standard, either by publication of an identical text or by endorsement, at the latest by June 1995, and conflicting national standards shall be withdrawn at the latest by June 1995.

This European standard supersedes EN 196-2:1987.

According to the CEN/CENELEC Internal Regulations the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, United Kingdom.

1 Scope

This European Standard describes the procedures for the chemical analysis of cement.

The standard describes the reference procedures and, in certain cases, an alternative method which can be considered as giving equivalent results.

If other methods are used it is necessary to show that they give results equivalent to those given by the reference methods. In the case of a dispute, only the reference procedures are used.

This standard applies to cements, and also to their constituent materials such as clinker and blastfurnace slag.

Standard specifications state which methods are to be used.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 196-7	*Methods of testing cement — Methods of taking and preparing samples of cement*
ISO 3534 : 1977	*Statistics — Vocabulary and symbols*

3 General requirements for testing

3.1 Number of tests

The number of tests for the various determinations (clauses 7 to 13) is fixed at two (see also 3.3).

3.2 Repeatability and reproducibility

The standard deviation of repeatability gives the closeness of agreement between successive results obtained with the same method on identical material tested under the same conditions (same operator, same apparatus, same laboratory and short time interval)[1].

The standard deviation of reproducibility gives the closeness of agreement between individual results obtained with the same method on identical material but tested under different conditions (different operators, different apparatus, different laboratories and/or different times)[1].

The standard deviations of repeatability and reproducibility are expressed in absolute %[2].

3.3 Expression of masses, volumes, factors and results

Express masses in grams to the nearest 0,0001 g and volumes from the burette in millilitres to the nearest 0,05 ml.

Express the factors of solutions, given by the mean of three determinations, to three decimal places.

Express the results of the tests, given by the mean of two determinations, as a percentage, generally to two decimal places.

If the difference between two determinations is more than twice the repeatability standard deviation, repeat the test and take the mean of the two closest values.

3.4 Ignitions

Carry out the ignitions as follows.

Place the filter paper and its contents into a crucible which has been previously ignited and tared. Dry it, then incinerate it slowly in an oxidising atmosphere, without flaming while ensuring complete combustion. Then ignite at the stated temperature. Allow the crucible and its contents to cool to the laboratory temperature in a desiccator. Weigh the crucible and its contents.

3.5 Determination of constant mass

Determine constant mass by making successive 15 min ignitions followed each time by cooling and then weighing. Constant mass is reached when the difference between two successive weighings is less than 0,0005 g.

3.6 Check for absence of chloride ions (silver nitrate test)

After generally five to six washes of a precipitate, rinse the base of the filter stem with a few drops of water. Wash the filter and its contents with several millilitres of water and collect this in a test tube. Add several drops of silver nitrate solution (4.33). Check the absence of turbidity or precipitate in the solution. If present, continue washing while carrying out periodic checks until the silver nitrate test is negative.

---

[1] Definitions taken from ISO 3534.

[2] The values of the standard deviation for repeatibility and standard deviation for reproducibility given in this standard shall be considered as provisional. These values will subsequently by stipulated according to experience acquired in the laboratories.

4 Reagents

4.0 General requirements

Use only reagents of analytical quality and distilled water, or water of equal purity, during the analysis.

Unless otherwise stated % means % by mass.

The concentrated liquid reagents used in this standard have the following densities (ρ) (in g/cm^3 at 20 °C):

hydrochloric acid	1,18 to 1,19
hydrofluoric acid	1,13
nitric acid	1,40 to 1,42
sulfuric acid	1,84
phosphoric acid	1,71 to 1,75
acetic acid	1,05 to 1,06
ammonium hydroxide	0,88 to 0,91
triethanolamine	1,12

The degree of dilution is always given as a volumetric sum, for example: hydrochloric acid 1 + 2 means that 1 volume of concentrated hydrochloric acid is to be mixed with 2 volumes of water.

4.1 *Concentrated hydrochloric acid (HCl).*

4.2 *Dilute hydrochloric acid 1 + 1.*

4.3 *Dilute hydrochloric acid 1 + 2.*

4.4 *Dilute hydrochloric acid 1 + 3.*

4.5 *Dilute hydrochloric acid 1 + 9.*

4.6 *Dilute hydrochloric acid 1 + 11.*

4.7 *Dilute hydrochloric acid 1 + 19.*

4.8 *Dilute hydrochloric acid 1 + 99.*

4.9 *Dilute hydrochloric acid of pH 1,60.* Add five or six drops of concentrated hydrochloric acid to 2 l water. Control the pH value by means of a pH-meter. Store the solution in a polyethylene flask.

4.10 *Concentrated hydrofluoric acid (HF).*

4.11 *Dilute hydrofluoric acid 1 + 3.*

4.12 *Nitric acid (HNO_3).*

4.13 *Concentrated sulfuric acid (H_2SO).*

4.14 *Dilute sulfuric acid 1 + 1.*

4.15 *Phosphoric acid (H_3PO_4).*

4.16 *Boric acid (H_3BO_3).*

4.17 *Acetic acid (CH_3COOH).*

4.18 *Amino-acetic acid (NH_2CH_2COOH).*

4.19 *Metallic chromium in powder form (Cr).*

4.20 *Concentrated ammonium hydroxide (NH_4OH.)*

4.21 *Dilute ammonium hydroxide 1 + 1.*

4.22 *Dilute ammonium hydroxide 1 + 10.*

4.23 *Dilute ammonium hydroxide 1 + 16.*

4.24 *Sodium hydroxide ($NaOH$).*

4.25 *Sodium hydroxide solution 4 mol/l.* Dissolve 160 g of sodium hydroxide in water and make up to 1000 ml. Store in a polyethylene flask.

4.26 *Sodium hydroxide solution 2 mol/l.* Dissolve 80 g of sodium hydroxide in water and make up to 1000 ml. Store in a polyethylene flask.

4.27 *Ammonium chloride (NH_4Cl).*

4.28 *Tin (II) chloride ($SnCl_2.2H_2O$).*

4.29 *Potassium periodate (KIO_4).*

4.30 *Sodium peroxide in powder form (Na_2O_2).*

4.31 *Mixture of sodium carbonate and sodium chloride.* Mix 7 g of sodium carbonate (anhydrous Na_2CO_3) with 1 g sodium chloride (NaCl).

4.32 *Barium chloride solution.* Dissolve 120 g of barium chloride ($BaCl_2.2H_2O$) in water and make up to 1000 ml.

4.33 *Silver nitrate solution.* Dissolve 5 g of silver nitrate ($AgNO_3$) in water, add 10 ml of concentrated nitric acid (HNO_3) and make up to 1000 ml with water.

4.34 *Sodium carbonate solution.* Dissolve 50 g of sodium carbonate (anhydrous Na_2CO_3) in water and make up to 1000 ml.

4.35 *Potassium hydroxide solution.* Dissolve 250 g of potassium hydroxide (KOH) in water and make up to 1000 ml.

4.36 *Ammoniacal zinc sulfate solution.* Dissolve 50 g of zinc sulfate ($ZnSO_4.7H_2O$) in 150 ml water and add 350 ml of concentrated ammonium hydroxide (NH_4OH). Leave to stand for at least 24 h and filter.

4.37 *Lead acetate solution.* Dissolve approximately 0,2 g of lead acetate $Pb(CH_3COO)_2.3H_2O$ in water and make up to 100 ml.

4.38 *Starch solution.* To 1 g of starch (water soluble), add 1 g of potassium iodide (KI), dissolve in water and make up to 100 ml.

4.39 *Polyethylene oxide solution*. Dissolve 0,25 g of polyethylene oxide $(-CH_2-CH_2-O-)_n$ of average molecular mass 200 000 to 600 000, in 100 ml water while stirring vigorously.

This solution is stable for approximately two weeks.

4.40 *Boric acid solution, saturated*. Dissolve approximately 50 g of boric acid (H_3BO_3) in water and make up to 1000 ml.

4.41 *Citric acid solution*. Dissolve 10 g of citric acid ($C_6H_8O_7.H_2O$) in water and make up to 100 ml.

4.42 *Ammonium molybdate solution*. Dissolve 10 g of ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ in water and make up to 100 ml.

Store the solution in a polyethylene flask. This keeps for approximately one week.

4.43 *Copper sulfate solution*. In a 50 ml volumetric flask dissolve 0,45 g of copper sulfate ($CuSO_4.5H_2O$) in water and make up to the mark.

4.44 *Ammonium acetate solution*. Dissolve 250 g of ammonium acetate (CH_3COONH_4) in water and make up to 1000 ml.

4.45 *Triethanolamine $N(CH_2CH_2OH)_3$ solution* 1 + 4.

4.46 *Reducing solution*. Dissolve successively in water 0,15 g of 1-amino-2-hydroxy naphthalene-4-sulfonic acid ($C_{10}H_9NO_4S$), 0,7 g of sodium sulfite (anhydrous Na_2SO_3) and 9,0 g of sodium metabisulfite ($Na_2S_2O_5$) and make up to 100 ml.

This solution will keep for a maximum of one week.

4.47 *Buffer solution of pH 1,40*. Dissolve 7,505 g of amino-acetic acid (NH_2CH_2COOH) and 5,850 g of sodium chloride (NaCl) in water and make up to 1000 ml. Dilute 300 ml of this solution to 1000 ml with dilute hydrochloric acid 1 + 99.

4.48 *Standard potassium iodate solution containing approximately 0,0166 mol/l*[3]. Dissolve successively, in freshly boiled and cooled water in a 1000 ml volumetric flask, (3,6 ± 0,1) g of potassium iodate (KIO_3, dried at 120 °C), two tablets of sodium hydroxide (NaOH) and 25 g of potassium iodide (KI). Make up to the mark with freshly boiled and cooled water.

The factor *F* of this solution is calculated from the following formula:

$$F = \frac{m_1}{3,5668} \qquad (1)$$

where m_1 is the mass of the portion of potassium iodate, in grams.

4.49 Sodium thiosulfate solution approximately 0,1 mol/l[3]

4.49.1 ***Preparation***

Dissolve 24,82 g of sodium thiosulfate ($Na_2S_2O_3.5H_2O$) in water and make up to 1000 ml. Before each test series, determine the factor *f* of this solution as described in **4.49.2.**

4.49.2 ***Standardization***

4.49.2.1 This standardization is carried out preferably in relation to the standard potassium iodate solution (4.48).

For this standardization, pipette 20 ml of the standard potassium iodate solution into a 500 ml conical flask and dilute with approximately 150 ml of water. Acidify with 25 ml of hydrochloric acid 1 + 1 and titrate with the approximately 0,1 mol/l sodium thiosulfate solution to a pale yellow colour.

Then add 2 ml of the starch solution (4.38) and continue the titration until the colour changes from blue to colourless.

The factor *f* of this solution is calculated from the formula:

$$f = \frac{20 \times 0,01667 \times 214,01 \times F}{3,5668 \times V_1} = 20 \times \frac{F}{V_1} \qquad (2)$$

where:

F	is the factor of the standard potassium iodate solution (4.48);
V_1	is the volume of the approximately 0,1 mol/l sodium thiosulfate solution used for the titration, in millilitres;
3,5668	is the mass of potassium iodate corresponding to a solution with exactly 0,01667 mol/l of potassium iodate, in grams;
214,01	is the molecular mass of KIO_3.

4.49.2.2 The standardization may also be carried out in relation to a known quality of potassium iodate.

For this standardization, place in a 500 ml conical flask (0,07 ± 0,005) g (m_2) of potassium iodate and dissolve in approximately 150 ml of water.

Add about 1 g of potassium iodide, acidify with 25 ml of hydrochloric acid 1 + 1 and titrate with the approximately 0,1 mol/l sodium thiosulfate solution until a pale yellow colour is obtained. Then add 2 ml of the starch solution (4.38) and titrate until the colour changes from blue to colourless.

---

[3] If the sulfide content is low (< 0,1 %), solutions ten times less concentrated should be used. They are prepared by pipetting 100 ml of the solutions 4.48 and 4.49 into 1000 ml volumetric flasks and making up to the mark with water.

The factor f of this solution is calculated from the formula:

$$f = \frac{1000 \times m_2}{3{,}5668 \times V_2} = 280{,}3634 \times \frac{m_2}{V_2} \qquad (3)$$

where:

- m_2 is the mass of the portion of potassium iodate, in grams;
- V_2 is the volume of the approximately 0,1 mol/l sodium thiosulfate solution used for the titration, in millilitres;
- 3,5668 is the mass of potassium iodate, in grams corresponding to a solution with exactly 0,01667 mol/l of potassium iodate.

4.50 Standard manganese ion solution

4.50.1 *Anhydrous manganese sulfate*

Dry some hydrated manganese sulfate ($MnSO_4.xH_2O$) to constant mass at a temperature of (250 ± 10) °C. The composition of the product obtained corresponds to the formula $MnSO_4$.

4.50.2 *Preparation*

Into a 1000 ml volumetric flask, weigh approximately 2,75 g of anhydrous manganese sulfate (m_3); dissolve in water and make up to the mark. The content G of manganese (II) ions of this solution, expressed in milligrams of Mn^{2+}/ml, is calculated from the formula:

$$G = \frac{m_3}{2{,}7485} \qquad (4)$$

where:

- m_3 is the mass of the portion of anhydrous manganese sulfate, in grams.

4.50.3 *Construction of the calibration graph*

Into each of two volumetric flasks, respectively 500 ml (No. 1) and 1000 ml (No. 2), pipette 20 ml of the standard manganese ion solution. Make up to the mark with water. Into each of three volumetric flasks, respectively 200 ml (No. 3), 500 ml (No. 4) and 1000 ml (No. 5) pipette 100 ml of the solution from flask No. 2 and make up to the mark with water.

Take 100 ml of each solution from flasks 1 to 5 and pipette each portion into a 400 ml beaker. Add 20 ml of concentrated nitric acid, 1,5 g of potassium periodate (4.29) and 10 ml of phosphoric acid (4.15), heat to boiling and boil gently for 30 min.

Cool to 20 °C and transfer the contents of each beaker to a 200 ml volumetric flask. Cool the flasks and their contents to 20 °C and make up to the mark with water. Measure the optical density of the solutions using a photometer (5.9) at a wavelength of around 525 nm, against water (use one or more cells (5.10) of appropriate sizes). Record the optical density values to three decimal places.

For each cell optical length plot a separate graph of the optical densities of these standard solutions E 1 to E 5 as a function of the corresponding manganese concentrations in milligrams of Mn per 200 ml. The corresponding manganese concentrations are given in table 1. They can be used as given if the content G obtained in accordance with 4.50.2 has the value 1,0000. Otherwise, multiply the manganese concentrations in table 1 by G.

Table 1. Concentrations of manganese standard solutions

Standard solution	E 1	E 2	E 3	E 4	E 5
Concentration of manganese in mg of Mn per 200 ml	4,0	2,0	1,0	0,4	0,2

4.51 Standard silica solution

4.51.1 *Silica (SiO_2)*, of purity > 99,9 % after ignition.

4.51.2 *Sodium carbonate*, anhydrous (Na_2CO_3).

4.51.3 *Basic solution*

Weigh 0,2000 g of silica, freshly ignited at (1175 ± 25) °C, in a platinum crucible already containing 2,0 g of sodium carbonate.

Heat the mixture and fuse it at a bright-red heat for at least 15 min. After cooling to room temperature, place the fused solid in a polyethylene beaker and dissolve it in water, then transfer the solution quantitatively to a 200 ml volumetric flask and make up to the mark with water.

Store the solution in a polyethylene bottle.

1 ml of solution contains 1 mg of SiO_2.

4.51.4 *Standard solution*

Pipette 5 ml of the basic solution into a 250 ml volumetric flask and make up to the mark with water. Store the solution in a polyethylene bottle. 1 ml of the solution contains 0,02 mg silica. This solution will keep for a maximum of one week.

4.51.5 *Compensating solutions*

Prepare the compensating solutions according to the procedure adopted for the silica content (13.3 to 13.5) by dissolving the amounts of the reagents given in table 2 in water and making up to 500 ml.

4.51.6 *Construction of the calibration curve*

Add from a burette the volumes of the silica calibration solution given in table 3 into 100 ml polyethylene beakers each containing a magnetic stirrer bar. Add 20 ml of the compensating solution by pipette and make up to 40 ml with water from a burette. The volumes required for this are also given in table 3. While stirring with a magnetic stirrer, add 15 drops of hydrofluoric acid 1 + 3. Stir for at least 1 min. Then pipette 15 ml of the boric acid solution (4.40) into the solution.

Table 2. Composition of the compensation solutions for a volume of 500 ml

		Precipitation by polyethylene oxide (13.3)	**Precipitation by double evaporation (13.4)**	**Decomposition by HCl and NH_4Cl (13.5)**
HCl conc.	ml	70	75	15
H_2SO_4 1 + 1	ml	1	1	–
HNO_3 conc.	ml	–	–	1
Polyethylene oxide solution	ml	5	–	–
NH_4Cl	g	–	–	1
Na_2CO_3	g	1,75	1,75	1,75
NaCl	g	0,25	0,25	0,25
Na_2O_2	g	3	3	–

Table 3. Composition of the silica calibration solutions and their silica content

Serial No.	Blank	1	2	3	4	5	6	7	8
Standard SiO_2 solution (ml)	0	2	4	5	6	8	10	15	20
Water (ml)	20	18	16	15	14	12	10	5	0
Silica content (mg SiO_2/100 ml)	0	0,04	0,08	0,10	0,12	0,16	0,20	0,30	0,40

Adjust the pH of the solution to (1,15 ± 0,05) by adding, drop by drop, either the sodium hydroxide solution (4.25), or hydrochloric acid 1 + 2. Carry out this operation with the aid of a pH meter calibrated using a buffer (4.47) with a neighbouring pH value (e.g. 1,40).

Pipette 5 ml of the ammonium molybdate solution (4.42) into the solution (time 0). Adjust the pH of this solution to 1,60 by adding, drop by drop, either the sodium hydroxide solution (4.25) or hydrochloric acid 1 + 2. Transfer the solution to a 100 ml volumetric flask rinsing with dilute hydrochloric acid of pH = 1,60 (4.9).

After 20 min, pipette 5 ml of the citric acid solution (4.41) into the volumetric flask, stir and leave to stand for 5 min.

Then pipette 2 ml of the reducing solution (4.46) into the volumetric flask. Make up to the mark with dilute hydrochloric acid pH = 1,60 (4.9) and mix thoroughly. Exactly 30 min after introducing the ammonium molybdate (time 0 + 30), measure the optical density with a photometer (5.9) using a cell of 1 cm optical length against the blank solution prepared in the same way, using the wavelength of maximum extinction near 815 nm. Construct a graph giving the measured optical densities as function of the corresponding silica contents given in table 3.

The blank solution used in constructing the calibration curve may be used as the blank solution here. The calibration curve enables the silica content in mg SiO_2/100 ml to be determined.

4.52 Standard calcium ion solution, approximately 0,01 mol/l

4.52.1 *Calcium carbonate ($CaCO_3$)*, dried at 200 °C of purity > 99,9 %.

4.52.2 *Standard solution*

Weigh approximately 1 g of calcium carbonate and place it in a 400 ml beaker with approximately 100 ml of water. Cover the beaker with a watch glass and carefully introduce approximately 10 ml of hydrochloric acid 1 + 2. After the reaction is completed, bring to boiling in order to expel the dissolved carbon dioxide. Cool and make up to 1000 ml in a volumetric flask.

4.53 EDTA solution, approximately 0,03 mol/l

4.53.1 *Dihydrated disodium salt of ethylenediaminetetra-acetic acid (EDTA)*

4.53.2 *Preparation*

Dissolve 11,17 g of EDTA in water and make up to 1000 ml. Store in a polyethylene bottle.

4.53.3 *Standardization*

Pipette 50 ml of the standard calcium ion solution (4.52) into a beaker suitable for the measuring apparatus (5.11). Then dilute with water to a volume suitable for the operation of the apparatus.

Using a pH meter, adjust the pH of this solution to 12,5 with the sodium hydroxide solution or solutions (4.25 and 4.26).

Determine the end-point using one of the following two methods.