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Water quality — Determination of selected parameters by discrete analysis systems —

Part 1: Ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate and silicate with photometric detection

Qualité de l'eau — Détermination de paramètres sélectionnés par des systèmes d'analyse discrète —

Partie 1: Ammonium, nitrate, nitrite, chlorure, orthophosphate, sulfate et silicate par détection photométrique

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2. www.iso.org/directives

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The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

ISO 15923 consists of the following parts, under the general title *Water quality — Determination of selected parameters by discrete analysis systems*:

— *Part 1: Ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate and silicate with photometric detection*

Introduction

Many photometric determinations can be automated with a discrete analysis system. With one single apparatus, a large number of different parameters can be determined, and the parameters to be determined can be specified for each sample. Working with small volumes requires less sample material and reagent.

Samples that fall beyond the normal measuring range can either be automatically diluted or measured again with a different measuring range.

This part of ISO 15923 specifies methods for the automatic determination of ammonium, nitrate, nitrite, chloride, orthophosphate, and silicate with photometric detection and a turbidimetric determination of sulfate using a discrete analysis system. The field of application is water (ground, potable, surface, waste, eluates, and boiler water).

Water quality — Determination of selected parameters by discrete analysis systems —

Part 1:
Ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate and silicate with photometric detection

WARNING — Persons using this part of ISO 15923 should be familiar with normal laboratory practice. This part of ISO 15923 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this part of ISO 15923 be carried out by suitably qualified staff.

1 Scope

This part of ISO 15923 specifies methods for the automatic performance of spectrophotometric and turbidimetric analyses with a discrete analysis system for determining ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate, and silicate. The field of application is ground, potable, surface, waste, eluates, and boiler water.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

3 Principle

A discrete analysis system is an automated system for spectrophotometric and turbidimetric determinations.

The colour reactions take place in reaction cells, which may be cuvettes, in an incubator. For each determination, a separate reaction cell is used. Preset volumes of the sample and the reagents are pipetted into the cells and mixed.

After expiry of the incubation period, the absorbance of the solution is measured at the wavelength applicable to the determination. This is done by passing the cuvettes through the photometer or by transferring the measuring solution from the reaction cells to a photometer with a flow-through cell.

4 Interferences

Particles present in the sample can lead to blockages and will interfere with the photometric measurement. Filtration of all samples through a 0,45 µm membrane filter is recommended, except for the determination of total phosphate and Kjeldahl nitrogen digests (see Annexes B and F). Particles can also be removed by settlement, centrifugation, or dialysis.

This method is applicable to samples in a pH range from 5 to 9, which covers most natural waters. Samples outside this range may require pH correction.

Inherent colour or turbidity of the sample interferes with the analysis. On the prevention of such interference, see Annex A. Interferences specific to each parameter are discussed in Annexes B to H.

NOTE Interference by inherent colour shall be compensated by measuring the absorbance of the sample before the addition of the chromogenic reagent (sample blanking) or by making use of a compensating solution (measuring solution without a chromogenic compound). For further details, see Annex A. A safe procedure for the correction of turbidity cannot really be given. The Lambert-Beer law does not apply to turbid solutions. Furthermore, many chromogenic reagents and coloured complexes are adsorbed on particles.

5 Reagents

Reagents for each parameter are specified in Annexes B to H. Use only reagents of recognized analytical grade, unless otherwise specified in the relevant annex. Dry all solid reagents for at least 1 h at (105 ± 5) °C, provided that they are thermally stable. Store the dried solid in a desiccator before weighing. Reagent volumes specified in Annexes B to H may be adjusted to suit local requirements or different instrument specifications.

5.1 Water, complying with grade 1 as defined in ISO 3696.

6 Apparatus

6.1 Discrete analysis system, generally consisting of the following components:

6.1.1 Sample injection device, for automated or manual operation.

6.1.2 Sample container.

6.1.3 Reagent container, refrigerated or not.

6.1.4 Incubator with temperature control, capable of maintaining a constant temperature of e.g. 37 °C.

6.1.5 UV/VIS detector, e.g. spectrophotometer, suitable for a wavelength range usually between 340 nm and 880 nm.

6.1.6 Control and data processing unit.

6.1.7 Recording device, e.g. PC with software for data acquisition and evaluation.

7 Sampling and sample preparation

Use clean vessels for sampling.

Turbidity or particulates interfere with spectrophotometric detection. Clarify samples by filtration through a 0,45 µm membrane (settlement, centrifugation, or dialysis may also be used). To avoid

contamination by the filter membrane, discard the first 20 ml to 30 ml of filtrate. Samples for the determination of total phosphate should not be filtered. Refer to Annex F.

Prepare and store the sample in accordance with Annexes B to H or with ISO 5667-3 if no specific guidance is given in the relevant annex.

Prepare a sample of water (5.1) in the same way as the sample, to be used as a blank.

Prepare a control standard solution from the primary control standard containing a level of analyte similar to the samples. Run as a sample at appropriate intervals in the batch, according to local requirements. A minimum interval of once every 20 samples is recommended.

8 Calibration

8.1 Calibration function

When the analytical system is first evaluated and at intervals afterwards, establish a calibration function for each parameter (see ISO 8466-1 or ISO 8466-2) as follows:

Using the primary calibration standard, prepare an appropriate series of calibration solutions for the respective parameter as described in Annexes B to H, including a zero-concentration solution.

Analyse the calibration solutions according to Clause 9 and the instrument manufacturer's instructions.

Confirm the validity of the data obtained and use to calculate the regression line as specified in ISO 8466-1 or ISO 8466-2.

Verify the continuing validity of the established calibration function by analysing an appropriate calibration standard solution, at regular intervals according to the accuracy requirements or at least at the end of the batch.

Recalibrate if necessary.

8.2 Calibration validity check

If the full calibration function is not established daily, carry out an initial calibration validity check by analysing two calibration standard solutions in the lower and upper third of the calibrated working range after the setup procedure (see Clause 9).

Verify the continuing validity of the established calibration function by analysing an appropriate calibration standard solution at regular intervals according to the accuracy requirements or at least at the end of the batch.

Recalibrate if necessary.

9 Procedure

Set up the discrete analysis system according to the instrument manufacturer's instructions.

Calibrate the system according to Clause 8 and the instrument manufacturer's instructions.

Prepare the samples according to Clause 7 and Annexes B to H. A consistent incubation temperature and time are essential for the stability of the absorbance measurements. For guidance on recommended incubation temperatures and times, refer to Annexes B to H. Note that the incubation times given in Annexes B to H are recommendations, which may be varied according to experience.

Measure the absorbance of the samples using the conditions in Annexes B to H and the instrument manufacturer's instructions. Measure the blank according to Annex A and the instrument manufacturer's instructions.

If the absorbance of the sample exceeds that of the top calibration solution, dilute the sample, or reduce the sample intake by an appropriate factor to bring it into the upper half of the calibration range, and reanalyse. If necessary, blank correct the sample absorbances (see Annex A).

The procedures in Annexes B to H may be modified for different instruments or to change the range or sensitivity of the method for different parameter concentrations or sample types.

10 Calculation

Calculate the mass concentration, ρ, of the parameter in question in micrograms per litre (µg/l) or milligrams per litre (mg/l) from the calibration line (see Clause 8), using the corrected absorbance values obtained (see Clause 9), as specified in ISO 8466-1 or ISO 8466-2. Take account of any dilution factors. This calculation can usually be carried out automatically using the instrument software.

11 Expression of results

Results shall be expressed to a maximum of three significant figures.

EXAMPLES Phosphate = 1,11 mg/l P (3 sig fig), 1,1 mg/l P (2 sig fig), 1 mg/l (1 sig fig).

Before reporting results, it is important to determine the required units of expression. For example, ammonium, nitrate, and nitrite can be expressed as N or as the relevant ion. Results for orthophosphate can be expressed as P or PO_4, and silicate may be expressed as SiO_4, SiO_2, or Si.

Appropriate conversion factors are given in Table 1.

Table 1 — Conversion factors

Parameter	Units	Conversion factor	Converted units
Ammonia	mg/l N	1,286	mg/l NH_4
Ammonia	mg/l NH_4	0,777 8	mg/l N
Nitrate	mg/l N	4,427	mg/l NO_3
Nitrate	mg/l NO_3	0,225 9	mg/l N
Nitrite	mg/l N	3,285	mg/l NO_2
Nitrite	mg/l NO_2	0,304 4	mg/l N
Orthophosphate	mg/l P	3,066	mg/l PO_4
Orthophosphate	mg/l PO_4	0,326 1	mg/l P
Silicate	mg/l Si	3,279	mg/l SiO_4
Silicate	mg/l SiO_4	0,305 0	mg/l Si
Silicate	mg/l Si	2,139	mg/l SiO_2
Silicate	mg/l SiO_2	0,467 4	mg/l Si
Silicate	mg/l SiO_2	1,533	mg/l SiO_4
Silicate	mg/l SiO_4	0,652 5	mg/l SiO_2

12 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this part of ISO 15923 (i.e. ISO 15923-1:2013);

b) the details required for identification of the sample;

c) the date of the analysis;

d) the analytical results (see Clause 11);

e) any deviation from this method and a report of circumstances that may have affected the results.

Annex A
(normative)

Correction for inherent colour

A.1 General

The two possibilities for the correction of inherent colour are described in A.2 and A.3. As a rule, it is not possible to correct for turbidity. In many cases, interference due to particles can be prevented by carefully filtering, settling, centrifuging, or dialysing samples.

A.2 Sample blanking

Sample blanking is possible only if reaction cells are used which also serve as cuvettes. The blank measurement is done after dispensing the sample and, if applicable, one or more reagents that could produce a colour change in the sample (for example, because of the influence of the pH on the colour of the sample), but before dispensing the chromogenic reagent. This blank value is subtracted from the final absorption of the measuring solution, taking into account the ratio between the volumes of the measuring solutions. The standards are measured in the same way.

A.3 Use of a compensating solution

When using a compensating solution, a second measuring solution is prepared that consists of the same volumes of sample and reagent, in which the compound responsible for forming the colour is omitted. This can be done by adding, instead of the chromogenic reagent, an equal volume of water or by preparing a separate reagent from which the chromogenic compound is omitted. The absorption of the compensating solution is deducted from the absorption of the sample solution.

Annex B
(normative)

Determination of ammonium

B.1 Principle

Ammonium reacts with hypochlorite, formed by alkaline hydrolysis of sodium dichloroisocyanurate, and with salicylate at a pH of approximately 12,6, in the presence of sodium nitroprusside as a catalyst, to produce a compound with a blue colour. The reagent contains citrate to mask interference by cations, such as calcium and magnesium ions. The absorbance at 660 nm is a measure of the ammonium content.

NOTE This method is based on the same chemistry given in ISO 7150-1.[5]

B.2 Interferences

Interference by cations, especially calcium and magnesium ions, is masked by citrate. In saline samples, this interference can nevertheless occur if the complexing capacity of the citrate is exceeded. This can be prevented by carrying out a distillation in accordance with ISO 7150-1.[5] Distillation is also advised for strongly coloured samples.

Extremely high or low pH values of the samples can interfere. Primary amines and components that can reduce hypochlorite can interfere with the determination, but these are rarely present in interfering concentrations in water samples. If the presence of any of these interferents is suspected in samples, the magnitude of the interference should be assessed prior to analysis.

B.3 Reagents

B.3.1 Nitric acid solution, $\rho(HNO_3)$, approximately 4 g/l.

Carefully add (4 ± 0,4) ml of concentrated nitric acid [HNO_3] to 800 ml of water in a graduated 1 l measuring flask and mix. Fill to the mark with water.

This solution is stable for 1 y if stored at room temperature.

B.3.2 Sodium nitroprusside reagent

In a 250 ml measuring flask, dissolve (32,5 ± 0,3) g of sodium salicylate [$C_7H_5O_3Na$] and (32,5 ± 0,3) g of sodium citrate [$C_6H_5Na_3O_7{\cdot}2H_2O$] in approximately 200 ml of water. Ensure that the pH is < 8,0. If necessary, acidify with nitric acid (B.3.1). Add (0,243 ± 0,002) g of sodium nitroprusside [$Na_2(Fe(CN)_5NO){\cdot}2H_2O$] and dissolve. Fill to the mark with water.

This solution is stable for 1 w in a dark bottle at 2 °C to 8 °C.

NOTE If necessary, add a suitable detergent, e.g polyoxyethylene lauryl ether, to prevent air bubbles from adhering to the wall of the cuvette while mixing the sample and reagents.

B.3.3 DIC reagent

In a 250 ml measuring flask, dissolve (8,0 ± 0,1) g of sodium hydroxide [NaOH] in approximately 200 ml of water and mix, leave to cool down and add (0,500 ± 0,005) g of sodium dichloroisocyanurate [$Cl_2Na(NCO)_3{\cdot}2H_2O$] and dissolve. Fill to the mark with water.

This solution is stable for 1 w in a dark bottle at 2 °C to 8 °C.

B.3.4 Primary calibration standard ammonium, ρ_N = 300 mg/l.

In a 1 l calibrated flask, dissolve (1,415 ± 0,001) g of ammonium sulfate [$(NH_4)_2SO_4$] in approximately 750 ml of water and fill to the mark with water.

This solution is stable for 3 mo at 2 °C to 8 °C.

B.3.5 Primary control standard ammonium, ρ_N = 200 mg/l.

Prepare the control standard using a different starting material to that used for the primary calibration standard.

Diammonium hydrogen citrate [$(NH_4)_2HC_6H_5O_7$], for example, can be used as a starting material.

In a 1 l calibrated flask, dissolve (1,615 ± 0,001) g diammonium hydrogen citrate in approximately 750 ml of water and fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

B.4 Procedure

B.4.1 Sample pretreatment

For the determination of the Kjeldahl nitrogen content, the samples shall first be digested.

NOTE ISO 5663[1] can be used for the digestion.

B.4.2 Calibration

The calibration curve is usually first order.

B.4.3 Analysis

The incubation temperature lies between 30 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— a maximum of 10 parts of sample by volume;

— 1 part of sodium nitroprusside reagent by volume (B.3.2). Mix the measuring solution after each addition;

— (1 ± 0,2) part of DIC reagent by volume (B.3.3). Mix the measuring solution after each addition. The recommended incubation time after the addition of the DIC reagent is 480 s.

After the incubation time, measure the absorbance at 660 nm.

NOTE A typical calibration range for this method is 0,05 mg/l N to 2,0 mg/l N.

Annex C
(normative)

Determination of the sum of nitrate and nitrite by the hydrazine method

C.1 Principle

Nitrate is reduced to nitrite with hydrazine sulfate. Both the nitrite produced by this reaction and the nitrite present in the sample then react with sulfanilamide and N-(1-naphtyl)ethylenediamine dihydrochloride (NED) to produce a diazide compound with a red colour.

The absorbance measured at 540 nm is a measure of the sum of the amount of nitrite and nitrate present.

NOTE 1 This method is based on the same chemistry in ISO 13395,[6] except that ISO 13395 uses a cadmium column for nitrate reduction (Note 3).

NOTE 2 With this method, the amount of fully oxidized nitrogen is determined. To obtain an accurate nitrate concentration, the amount of nitrite must be subtracted. Nitrite is determined by omitting the hydrazine reduction step from the method. Refer to Annex D.

NOTE 3 Nitrate can also be reduced to nitrite with a cadmium column in place of hydrazine sulfate.

C.2 Interference

Sulfide concentrations of 10 mg/l can cause a 10 % negative deviation in the result. Chloride in excess of 100 mg/l may also cause negative bias. Nitrate is converted to nitrite prior to determination. Refer to D.2 for further discussion of interferences.

C.3 Reagents

C.3.1 **Copper sulfate solution**, ρ = 3,9 g/l.

In a 100 ml measuring flask, dissolve (0,39 ± 0,01) g of copper sulfate [$CuSO_4 \cdot 5H_2O$] in 100 ml of water. This solution is stable for 6 mo if stored at room temperature.

C.3.2 **Zinc sulfate solution**, ρ = 45 g/l.

In a 100 ml measuring flask, dissolve (4,5 ± 0,1) g of zinc sulfate [$ZnSO_4 \cdot 7H_2O$] in 100 ml of water.

This solution is stable for 6 mo at room temperature.

C.3.3 **Sodium hydroxide solution**, ρ = 8 g/l.

In a 100 ml measuring flask, dissolve (0,80 ± 0,04) g of sodium hydroxide [NaOH] in 100 ml of water.

This solution is stable for at least 1 w if stored in a closed vessel.

NOTE If necessary, add a suitable detergent, e.g. polyoxyethylene lauryl ether, to prevent air bubbles from adhering to the wall of the cuvette while mixing the sample and reagents. To reduce problems with Ca and Mg precipitation, 0,3 ml phosphoric acid (85 %) may be added to the sodium hydroxide solution.

C.3.4 Reduction reagent

In a 250 ml measuring flask, dissolve (0,163 ± 0,001) g of hydrazine sulfate [$N_2H_4 \cdot H_2SO_4$] in approximately 200 ml of water. Add (0,375 ± 0,005) ml of copper sulfate solution (C.3.1) and (2,50 ± 0,05) ml of zinc sulfate solution (C.3.2) and fill to the mark with water.

This solution is stable for 2 w if stored at 2 °C to 8 °C.

The optimum hydrazine concentration of the reduction solution can differ per lot and shall be determined when a new lot is used.

Determine the reduction yield by analysing a nitrate and a nitrite solution with the same N concentration which is approximately 100 % of the NO_3-N measuring range. The absorbance of the nitrate solution should be between 95 % and 110 % of the absorbance of the nitrite solution. If the absorbance of the nitrate is lower than that of the nitrite solution, the nitrate conversion is not complete. The hydrazine content must be increased until the absorbance is within this range.

C.3.5 NED reagent

In a 1 l measuring flask, carefully add 50 ml of phosphoric acid [H_3PO_4] (85 %) to 500 ml of water. Add (5,0 ± 0,1) g of sulfanilamide [$C_6H_8N_2O_2S$] and dissolve. Add (0,25 ± 0,01) g N-(1-naphtyl)ethylenediamine dihydrochloride [$C_{12}H_{16}Cl_2N_2$] (NED), dissolve, and fill to the mark with water.

This solution is stable for 1 mo if stored in a dark bottle at 2 °C to 8 °C.

C.3.6 Primary calibration standard nitrate, ρ_N = 600 mg/l

Desiccate potassium nitrate [KNO_3] for at least 2 h at (105 ± 5) °C. Cool in an exsiccator for at least 45 min and dissolve (4,331 ± 0,001) g in a 1 l measuring flask in approximately 750 ml of water. Fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

C.3.7 Primary control standard nitrate, ρ_N = 400 mg/l

Prepare the control standard using a different starting material to that used for the primary calibration standard.

Sodium nitrate [$NaNO_3$], for example, can be used as a starting material.

Desiccate sodium nitrate for 2 h at (105 ± 5) °C. Cool in an exsiccator for 45 min and dissolve (2,427 ± 0,001) g in a 1 l measuring flask in approximately 750 ml of water. Fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

C.4 Procedure

C.4.1 Calibration

The calibration curve is usually first order.

C.4.2 Analysis

The incubation temperature lies between 30 °C and a maximum of 40 °C. Prepare a measuring solution typically made up of the following:

— 1 part of sodium hydroxide solution by volume (C.3.3);

— (1 ± 0,1) parts of sample by volume. Mix the solution after each addition. The recommended incubation time after the addition of the sample is 180 s;

— (1 ± 0,2) part of reduction reagent by volume (C.3.4). Mix the solution after each addition. The recommended incubation time after the addition of the TON-2 reagent is 420 s;

— (1 ± 0,5) part of NED reagent (C.3.5) by volume. Mix the solution after each addition. The recommended incubation time after the addition of the NED reagent is 300 s.

After the last incubation, measure the absorbance at 540 nm.

NOTE A typical calibration range for this method is 0,1 mg/l N to 6,0 mg/l N.

To determine nitrate, subtract the nitrite value (see Annex D) from the result obtained using this procedure.

Annex D
(normative)

Determination of nitrite

D.1 Principle

In an acid environment, nitrite reacts with sulfanilamide and naphthyl ethylenediamine (NED) to form a diazide compound with a red colour. The absorbance at 540 nm is a measure of the nitrite content.

NOTE This method is based on the same chemistry given in ISO 6777.[3]

D.2 Interference

High alkalinity interferes. Samples with hydrogen carbonate alkalinity > 300 mg/l may require dilution or addition of phosphoric acid prior to analysis to ensure a pH of 1,9 after treatment with chromogenic reagent. Free chlorine, chloramines, and high levels of polyphosphate, iron(III), or thiosulfate may also interfere. If the presence of any of these interferents is suspected in samples, the magnitude of the interference should be assessed prior to analysis.

D.3 Reagents

D.3.1 NED reagent

In a 1 l measuring flask, carefully add 50 ml of phosphoric acid [H_3PO_4] (85 %) to 500 ml of water. Add (5,0 ± 0,1) g of sulfanilamide [$C_6H_8N_2O_2S$] and dissolve. Add (0,25 ± 0,01) g of N-(1-naphtyl) ethylenediamine dihydrochloride [$C_{12}H_{16}Cl_2N_2$], dissolve, and fill to the mark with water.

This solution is stable for 1 mo if stored in a dark bottle at 2 °C to 8 °C.

D.3.2 Primary calibration standard nitrite, ρ_N = 200 mg/l.

Desiccate sodium nitrite [$NaNO_2$] for 1 h at (105 ± 5) °C. Cool in an exsiccator for 45 min and dissolve (0,985 ± 0,001) g in a 1 l measuring flask in approximately 750 ml of water. Fill to the mark with water.

This solution is stable for 1 mo at 2 °C to 8 °C.

D.3.3 Primary control standard nitrite, ρ_N = 125 mg/l.

Prepare the control standard using a different starting material to that used for the primary calibration standard.

Potassium nitrite [KNO_2], for example, can be used as a starting material.

Desiccate for at least 2 h at (105 ± 5) °C. Cool in an exsiccator for at least 45 min and dissolve (0,759 ± 0,001) g in a 1 l measuring flask in approximately 750 ml of water and fill to the mark with water.

This solution is stable for 3 mo at 2 °C to 8 °C.

D.4 Procedure

D.4.1 Calibration

The calibration curve is usually first order.

D.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— a maximum of 5 parts of sample by volume;

— 1 part of NED reagent by volume (D.3.1). The recommended incubation time after adding NED reagent is least 360 s. Mix the solution after each addition.

After incubation, measure the absorbance at 540 nm.

NOTE 1 A typical calibration range for this method is 0,01 mg/l N to 0,6 mg/l N.

NOTE 2 A compensating solution for inherent colour can be prepared by omitting the sulphanilamide and N-(1-naphtyl)ethylenediamine dihydrochloride from the NED reagent (D.3.1). Refer also to Annex A.

Annex E
(normative)

Determination of chloride by the thiocyanate method

E.1 Principle

Chloride reacts with mercury(II) thiocyanate to form non-ionized (but soluble) mercury(II) chloride and an equivalent amount of free thiocyanate, which forms a red complex with iron(III).

This method is based on the same chemistry given in ISO 15682.[7]

The absorbance at 480 nm is a measure of the chloride content.

E.2 Interference

Compounds that liberate free thiocyanate from mercury(II) thiocyanate, e.g. bromide and iodide, will interfere. Bromide causes a significant interference above 30 mg/l. If the concentration of interferent is known, it can be accounted for in the calculation. Sulfide interferes and can be eliminated by adding 5 ml of 30 % hydrogen peroxide (commercially available). The magnitude of any suspected interference should be assessed prior to analysis.

E.3 Reagents

E.3.1 **Mercury thiocyanate solution**, ρ = 4,16 g/l.

In a 100 ml measuring flask, dissolve (0,416 ± 0,001) g of mercury thiocyanate [$Hg(SCN)_2$] in 100 ml of methanol. Mix and filter if necessary.

This solution is stable for 3 mo if stored in a dark bottle at room temperature.

E.3.2 **Iron nitrate solution**, ρ = 202 g/l.

In a 100 ml measuring flask, dissolve (20,2 ± 0,1) g of iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] in 50 ml of water. Carefully add (4,44 ± 0,04) ml of concentrated nitric acid. Fill to the mark with water.

This solution is stable for 3 mo if stored in a dark bottle at room temperature.

E.3.3 **Chromogenic reagent**, Cl.

Measure (75 ± 1) ml of mercury thiocyanate solution and (75 ± 1) ml of iron nitrate solution into a 500 ml measuring flask. Fill to the mark with water and mix.

This solution is stable for 3 mo in a dark bottle at room temperature.

E.3.4 **Primary calibration standard chloride**, ρ = 50 g/l.

Desiccate sodium chloride [NaCl] for 4 h at (105 ± 5) °C. Cool in an exsiccator for 45 min and dissolve (41,21 ± 0,01) g in a 500 ml measuring flask in approximately 350 ml of water and fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

E.3.5 Primary control standard chloride, ρ = 15 g/l.

Prepare the control standard using a different starting material to that used for the primary calibration standard.

Potassium chloride [KCl], for example, can be used as a starting material.

Desiccate for at least 2 h at (105 ± 5) °C. Cool in an exsiccator for at least 45 min and dissolve (31,54 ± 0,01) g in a 1 l measuring flask in approximately 250 ml of water and fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

E.4 Procedure

E.4.1 Calibration

The calibration curve is usually second order.

E.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— 6 parts of chromogenic reagent, Cl by volume (E.3.3). The incubation time after adding chromogenic reagent, Cl, is at least 240 s;

— a maximum of 1 part of sample by volume. The recommended incubation time after the addition of the sample to the reagent is 180 s.

After the last incubation, measure the absorbance at 480 nm.

NOTE A typical calibration range for this method is 5 mg/l Cl to 400 mg/l Cl.

Annex F
(normative)

Determination of orthophosphate

F.1 Principle

Phosphate reacts with molybdate and antimony potassium tartrate in an acid environment. The complex thus formed is converted into a compound with a blue colour by reduction with ascorbic acid. The absorbance at 880 nm is a measure of the orthophosphate content.

NOTE This method is based on the same chemistry given in ISO 6878.[4]

F.2 Interference

Arsenate produces a similar colour to orthophosphate. This interference can be eliminated by reducing arsenate to arsenite. High concentrations of silicate (> 5 mg/l), sulfide (> 2 mg/l), nitrite (> 3 mg/l), chromium, iron and copper (> 10 mg/l) may also interfere. If the presence of any of these interferents is suspected in samples, the magnitude of the interference should be assessed prior to analysis.

F.3 Reagents

F.3.1 **Ammonium molybdate solution**, ρ = 40 g/l.

In a 100 ml measuring flask, dissolve (4,0 ± 0,1) g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$] in 100 ml of water.

This solution is stable for 1 mo if stored in a polyethene bottle at 2 °C to 8 °C.

F.3.2 **Potassium antimony tartrate solution**, ρ = 3,2 g/l.

In a 50 ml measuring flask, dissolve (0,16 ± 0,01) g of potassium antimony(III) oxide tartrate trihydrate [$C_8H_4K_2O_{12}Sb_2{\cdot}3H_2O$] in 50 ml of water.

This solution is stable for 2 mo if stored in a polyethene bottle at 2 °C to 8 °C.

F.3.3 **Sulfuric acid solution**, ρ (H_2SO_4) approximately 250g/l.

Carefully add (70 ± 2) ml of concentrated sulfuric acid [H_2SO_4] to 400 ml of water in a 500 ml beaker and fill to approximately 500 ml.

This solution is stable for 1 y if stored at room temperature.

F.3.4 **Ascorbic acid solution**, ρ = 18 g/l.

In a 250 ml measuring flask, dissolve (4,5 ± 0,1) g of ascorbic acid [$C_6H_8O_6$] in 250 ml of water.

This solution is stable for 1 w if stored in a polyethene bottle at 2 °C to 8 °C.

F.3.5 **Molybdate-tartrate reagent**.

In a polyethene bottle, add 75 ml of ammonium molybdate solution (F.3.1) to 250 ml of sulfuric acid solution (F.3.3). Then add 25 ml potassium antimony tartrate solution (F.3.2).

This solution is stable for 2 mo if stored in a polyethene bottle in the refrigerator.

F.3.6 Chromogenic reagent, PO_4.

In a reagent container, mix (14 ± 0,5) ml of molybdate-tartrate reagent (F.3.5) with (6 ± 0,2) ml ascorbic acid solution (F.3.4).

Prepare the solution freshly on the day of use.

F.3.7 Primary calibration standard phosphate, ρ (P) = 100 mg/l.

Desiccate potassium dihydrogen phosphate [KH_2PO_4] for 2 h at (105 ± 5) °C. Cool in an exsiccator for 45 min and dissolve (0,439 ± 0,001) g in a 1 l measuring flask in approximately 750 ml of water. Fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

F.3.8 Primary control standard phosphate, ρ (P) = 30 mg/l.

Prepare the control standard using a different starting material to that used for the primary calibration standard.

Disodium hydrogen phosphate [Na_2HPO_4], for example, can be used as a starting material.

Desiccate disodium hydrogen phosphate for 2 h at (105 ± 5) °C. Cool in an exsiccator for 45 min and dissolve (0,1375 ± 0,0002) g in a 1 l measuring flask in approximately 750 ml of water. Fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

F.4 Procedure

F.4.1 Sample pretreatment

For the determination of the total phosphate content, the samples shall first be digested by an appropriate method.

NOTE ISO 6878[4] can be used for the digestion.

F.4.2 Calibration

The calibration curve is usually first order.

F.4.3 Analysis

The incubation temperature lies between 30 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— 6 parts of sample by volume;

— 1 part of chromogenic reagent, PO_4 per 6 parts of sample volume fraction (F.3.6). Mix the solution after each addition. The recommended incubation time after adding chromogenic reagent, PO_4, is 540 s.

After incubation, measure the absorbance at 880 nm.

NOTE 1 The ratio between the sample and the reagent must be kept constant or the final pH value will be incorrect. This will result in loss of sensitivity.

NOTE 2 The absorbance can also be measured at 660 nm with a lower sensitivity.

NOTE 3 A typical calibration range for this method is 0,01 mg/l P to 1,00 mg/l P.

NOTE 4 A suitable compensating solution for inherent colour is sulfuric acid solution (F.3.3) diluted 1:1 with water. Refer also to Annex A.

Annex G
(normative)

Determination of sulfate by the turbidimetric method

G.1 Principle

Sulfate forms a precipitate with barium chloride in an acid environment. The resulting turbidity of the solution is measured at 540 nm and is a measure of the sulfate content.

G.2 Interference

High concentrations of carbonate, hydrogen carbonate, and chloride can interfere with the determination. Silica at concentrations > 500 mg/l will interfere. Differences can also occur with highly coloured and/or turbid samples. If the presence of any of these interferents is suspected in samples, the magnitude of the interference should be assessed prior to analysis.

G.3 Reagents

G.3.1 Turbidimetric reagent.

In a beaker, dissolve approximately 0,125 g of gelatine in hot water (approximately 80 °C) and mix for at least 1 h. Cool and transfer to a 500 ml measuring flask. Add (5,0 ± 0,1) g of barium chloride [$BaCl_2 \cdot 2H_2O$] and (5,0 ± 0,1) g of sodium chloride [NaCl]. Then carefully add (2,5 ± 0,1) ml of concentrated hydrochloric acid and fill to the mark with water.

This solution is stable for 1 w if stored at 2 °C to 8 °C.

G.3.2 Primary calibration standard sulfate, ρ = 2 000 mg/l.

Desiccate sodium sulfate [Na_2SO_4] for 2 h at (105 ± 5) °C. Dissolve (2,957 ± 0,001) g in a 1 l measuring flask in approximately 250 ml of water and fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

G.3.3 Primary control standard sulfate, ρ = 150 mg/l.

Prepare the control standard using a different starting material to that used for the primary calibration standard.

Ammonium sulfate [$(NH_4)_2SO_4$], for example, can be used as a starting material.

Desiccate ammonium sulfate for 2 h at (105 ± 5) °C. Dissolve (0,2063 ± 0,0002) g in a 1 l measuring flask in approximately 250 ml of water and fill to the mark with water.

This solution is stable for 3 mo if stored at 2 °C to 8 °C.

G.4 Procedure

G.4.1 Calibration

The calibration curve is usually second order.