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Water quality — Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) —

Part 2: Method by continuous flow analysis (CFA)

Qualité de l'eau — Dosage des orthophosphates et du phosphore total par analyse en flux (FIA et CFA) —

Partie 2: Méthode par analyse en flux continu (CFA)

Reference number
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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15681-2 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

ISO 15681 consists of the following parts, under the general title *Water quality — Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA)*:

— *Part 1: Method by flow injection analysis (FIA)*

— *Part 2: Method by continuous flow analysis (CFA)*

Introduction

Methods of determining water quality using flow analysis automated wet chemical procedures and are particularly suitable for the processing of many analytes in water in large sample series at a high analysis frequency.

Analysis can be performed by flow injection analysis (FIA) [1], [2] or continuous flow analysis (CFA) [3]. Both methods share the feature of an automatic dosage of the sample into a flow system (manifold) where the analyte in the sample reacts with the reagent solutions on its way through the manifold. The sample preparation may be integrated in the manifold. The amount of reaction product is measured in a flow detector (e.g. flow photometer). This part of ISO 15681 describes the CFA method.

The user should be aware that particular problems could require the specification of additional marginal conditions.

Water quality — Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) —

Part 2: Method by continuous flow analysis (CFA)

WARNING — Persons using this part of ISO 15681 should be familiar with normal laboratory practice. This part of ISO 15681 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. Molybdate and antimony waste solutions should be disposed of properly. It is absolutely essential that tests conducted according to this part of ISO 15681 be carried out by suitably qualified staff.

1 Scope

This part of ISO 15681 specifies CFA methods for the determination of orthophosphate in the mass concentration range from 0,01 mg/l to 1,00 mg/l P, and total phosphorus in the mass concentration range from 0,10 mg/l to 10,0 mg/l P. The method includes the digestion of organic phosphorus compounds and the hydrolysis of inorganic polyphosphate compounds, performed either manually as described in ISO 6878 [5], [6] or with an integrated UV digestion and hydrolysis unit.

This part of ISO 15681 is applicable to various types of water (such as ground, drinking, surface, leachate and waste water). The range of application may be changed by varying the operating conditions.

This method is also applicable to the analysis of seawater, but with changes in sensitivity, by adaptation of the carrier and calibration solutions to the salinity of the samples.

2 Normative references

The following referenced documents are indispensable for the application of this document. 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 — Specifications and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design on sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

ISO 6878:—[1)], *Water quality — Determination of phosphorus — Ammonium molybdate spectrometric method*

1) To be published.

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*

3 Interferences

3.1 General interferences

ISO 6878:—, Annex B gives a list of general interferences. In addition, or contrary to the cited standard, the following guidelines apply.

a) Arsenate causes serious interference. 100 µg/l As, present as arsenate, results in a response comparable to approximately 30 µg/l P.

b) If the silicate concentration in samples is not greater than 60 times the phosphorus concentration, interferences by silicate can be neglected.

c) Fluoride interference is significant above 50 mg/l.

d) Nitrite interference is significant above 5 mg/l. The interference can be eliminated by acidifying samples after collection.

e) For samples containing high concentrations of oxidizing agents, the amount of added reduction reagent can be insufficient. In this case, remove the oxidizing material prior to digestion.

f) The self-absorption of the sample can be compensated by measuring, in addition to the sample signal (8.6), the signal of the sample without the admixture of the reagents. In this case, the difference of the two responses is used for the evaluation (Clause 9).

3.2 Interferences in the determination of total-P

Samples containing solids or suspended particles can show low values when analysed by the UV method, if the particles are not completely transported into the UV unit. The error can be minimized by stirring the sample immediately before sampling, in order to ensure that a representative sample is delivered into the analyser, and by reducing the particle size.

The interferences from silicate, nitrite, fluoride and iron described for the orthophosphate determination are generally not observed in the UV method, due to the pre-digestion and the higher analytical range.

The efficiency of the UV digestion can be affected for water samples with chemical oxygen demand (COD) values of more than 10 times the highest concentrations of the calibration solutions (5.21). In this case, the sample should be diluted.

4 Principle

4.1 Determination of orthophosphate

The sample is mixed with a surfactant solution, followed by an acidic solution containing molybdate and antimony ions. The resulting phospho-antimony-molybdate complex is reduced by ascorbic acid to molybdenum blue [4], [5].

4.2 Total phosphorus with manual digestion

Phosphorus compounds in the sample are oxidized manually with a potassium peroxodisulfate solution, in accordance with ISO 6878, or with an equivalent procedure. The resulting orthophosphate is determined by the molybdenum blue reaction using the colour reaction described in 4.1. The samples can be neutralized manually according to ISO 6878 or by taking into account the amount of acid used in this procedure when calculating the acid to be used in the molybdenum reagent.

4.3 Total phosphorus with integral UV digestion and hydrolysis

The sample is mixed with potassium peroxodisulfate and passed through a UV digestor, followed by acid digestion to hydrolyse polyphosphates. The resulting orthophosphate is measured using the colour reaction described in 4.1.

5 Reagents

Use analytical grade chemicals unless otherwise specified.

5.1 Water complying to grade 1 of ISO 3696.

The phosphate blank value shall be checked (8.3).

5.2 Sulfuric acid, H_2SO_4.

5.2.1 Sulfuric acid (I), $\rho = 1{,}84$ g/ml; 98 % (mass fraction).

5.2.2 Sulfuric acid (II), $c(H_2SO_4) = 2{,}45$ mol/l.

To approximately 800 ml of water (5.1), carefully add 136 ml of sulfuric acid (I) (5.2.1) while stirring. Cool and dilute to 1 000 ml with water (5.1).

5.3 Ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$.

5.4 Antimony potassium tartrate hemihydrate, $K(SbO)C_4H_4O_6 \cdot 0{,}5\ H_2O$.

5.5 Ascorbic acid, $C_6H_8O_6$.

5.6 Sodium dodecyl sulfate, $NaC_{12}H_{25}SO_4$.

5.7 Potassium peroxodisulfate, $K_2S_2O_8$.

5.8 Potassium dihydrogen phosphate, KH_2PO_4, dried at 105 °C ± 5 °C to constant mass.

5.9 Potassium pyrophosphate, $K_4P_2O_7$.

5.10 Organophosphorus compounds to check the UV digestion.

5.10.1 Pyridoxal-5-phosphate monohydrate, $C_8H_{10}NO_6P \cdot H_2O$ *or alternatively*:

5.10.2 Disodium phenylphosphate, $C_6H_5Na_2PO_4$.

5.11 Surfactant solutions

5.11.1 Surfactant solution I, [see (A) in Figure A.1].

Dissolve 1 g of sodium dodecyl sulfate (5.6) in about 800 ml of water (5.1) and dilute to 1 000 ml.

The solution is stable for 6 months if stored at room temperature.

5.11.2 Surfactant solution II, [see (B) in Figure A.1, and S1 in Figure A.2].

Dissolve 10 g of sodium dodecyl sulfate (5.6) in about 800 ml of water (5.1) and dilute to 1 000 ml.

The solution is stable for 6 months if stored at room temperature.

5.12 Molybdate solution

Dissolve 40 g of ammonium heptamolybdate tetrahydrate (5.3) in about 800 ml of water (5.1) and dilute to 1 000 ml with water (5.1).

The solution is stable for 3 months if stored at room temperature.

5.13 Antimony potassium tartrate solution

Dissolve 2,5 g of antimony potassium tartrate hemihydrate (5.4) in about 800 ml of water (5.1) and dilute to 1 000 ml with water (5.1).

The solution is stable for 3 months if stored at room temperature.

5.14 Antimony tartrate molybdate reagents

5.14.1 Antimony tartrate molybdate reagent I, for determination of orthophosphate and total P after manual digestion (R1 in Figure A.1).

Mix 500 ml of sulfuric acid (II) (5.2.2), 150 ml of molybdate solution (5.12) and 50 ml of antimony potassium tartrate solution (5.13).

The solution is stable for 2 weeks if stored at room temperature.

5.14.2 Antimony tartrate molybdate reagent II, for total phosphorus determination after integrated UV digestion (R3 in Figure A.2).

Dissolve 20 g of ammonium heptamolybdate tetrahydrate (5.3) and 50 mg of antimony potassium tartrate hemihydrate (5.4) in about 800 ml of water (5.1), add 100 ml of surfactant solution II (5.11.2) and bring to a volume of 1 000 ml with water (5.1).

The solution is stable for 2 weeks if stored at room temperature.

5.15 Ascorbic acid solution I, (R2 in Figure A.1).

Dissolve 1 g of ascorbic acid (5.5) in about 80 ml of water (5.1) and bring to a volume of 100 ml with water (5.1). Store in the dark. Prepare the solution daily before use.

5.16 Ascorbic acid solution II, (R4 in Figure A.2).

Dissolve 3,5 g of ascorbic acid (5.5) in about 80 ml of water (5.1), add 0,1 g of sodium dodecyl sulfate (5.6) and dilute with water (5.1) to 100 ml. Store in the dark. Prepare the solution daily before use.

5.17 Digestion reagents for the determination of total phosphorus after integrated UV digestion.

5.17.1 Digestion reagent I, working range 0,10 mg/l to 1,00 mg/l [line (D) in Figure A.2].

Dissolve 10 g of potassium peroxodisulfate (5.7) in about 600 ml of water (5.1). While stirring, carefully add 340 ml of sulfuric acid (II) (5.2.2), cool and dilute with water (5.1) to 1 000 ml.

The solution is stable for 2 weeks if stored at room temperature.

5.17.2 Digestion reagent II, working range 1,00 mg/l to 10,0 mg/l [line (C) in Figure A.2].

Dissolve 2,5 g of potassium peroxodisulfate (5.7) in about 600 ml of water (5.1). While stirring, carefully add 85 ml of sulfuric acid (II) (5.2.2), cool and dilute with water (5.1) to 1 000 ml.

The solution is stable for 2 weeks if stored at room temperature.

5.18 Orthophosphate stock solution I, $\rho = 50{,}0$ mg/l orthophosphate-P.

Dissolve 220 mg $\pm$ 1 mg of potassium dihydrogenphosphate (5.8) in water (5.1) and dilute with water (5.1) to 1 000 ml. Store in a tightly closed glass bottle.

The solution is stable for 2 months if stored at 4 °C $\pm$ 2 °C.

5.19 Orthophosphate stock solution II, $\rho = 10{,}0$ mg/l P.

Dilute 20 ml of solution (5.18) to 100 ml with water (5.1). Prepare fresh daily.

5.20 Orthophosphate stock solution III, $\rho = 1{,}00$ mg/l P.

Dilute 2 ml of solution (5.18) to 100 ml with water (5.1). Prepare fresh daily.

5.21 Calibration solutions.

Prepare at least five calibration solutions by diluting solutions 5.18 to 5.20 according to the range required.

Ranges:

For orthophosphate-P:	range II:	0,01 mg/l to 0,10 mg/l P
	range I:	0,10 mg/l to 1,00 mg/l P
For total-P:	range II:	0,10 mg/l to 1,00 mg/l P
	range I:	1,00 mg/l to 10,0 mg/l P

Tables 1 to 3 give examples for the preparation of 10 calibration solutions for the above-mentioned ranges.

Table 1 — Example for the preparation of 10 calibration solutions for the orthophosphate range II (0,01 mg/l to 0,10 mg/l P)

Millilitres of orthophosphate stock solution III (5.20) diluted to 100 ml	1	2	3	4	5	6	7	8	9	10
Concentration of calibration solutions, mg/l P	0,01	0,02	0,03	0,04	0,05	0,06	0,07	0,08	0,09	0,10

Table 2 — Example for the preparation of 10 calibration solutions for the orthophosphate range I and total phosphorus range II (0,10 mg/l to 1,00 mg/l P)

Millilitres of orthophosphate stock solution II (5.19) diluted to 100 ml	1	2	3	4	5	6	7	8	9	10
Concentration of calibration solutions, mg/l P	0,10	0,20	0,30	0,40	0,50	0,60	0,70	0,80	0,90	1,00

Table 3 — Example for the preparation of 10 calibration solutions for the total phosphorus range I (1,00 mg/l to 10,0 mg/l P)

Millilitres of orthophosphate stock solution I (5.18) diluted to 100 ml	2	4	6	8	10	12	14	16	18	20
Concentration of calibration solutions, mg/l P	1,00	2,00	3,00	4,00	5,00	6,00	7,00	8,00	9,00	10,0

Prepare the calibration solutions immediately before use.

5.22 Standards for verifying hydrolysis and digestion efficiency

5.22.1 Potassium pyrophosphate stock solution, $\rho = 100$ mg/l P.

Dissolve 533 mg $\pm$ 3 mg of potassium pyrophosphate (5.9) in about 800 ml of water (5.1) and dilute with water (5.1) to 1 000 ml. Store in a sealed glass container at 4 °C $\pm$ 2 °C.

The solution is stable for 6 months.

5.22.2 Potassium pyrophosphate solution I, to check hydrolysis efficiency, $\rho = 0{,}50$ mg/l P, for the total-P working range II (0,10 mg/l to 1,00 mg/l P).

Dilute 0,5 ml of solution 5.22.1 and 100 µl of sulfuric acid (II) (5.2.2) to 100 ml with water (5.1).

The solution is stable for 1 month if stored at 4 °C $\pm$ 2 °C.

5.22.3 Potassium pyrophosphate solution II, to check hydrolysis efficiency, $\rho = 5{,}00$ mg/l P for the total-P working range I (1,00 mg/l to 10,0 mg/l P).

Dilute 5 ml of solution 5.22.1 and 100 µl of sulfuric acid (II) (5.2.2) to 100 ml with water (5.1).

The solution is stable for 1 month if stored at 4 °C $\pm$ 2 °C.

5.22.4 Organophosphorus stock solution, $\rho = 100$ mg/l P.

Dissolve 856 mg $\pm$ 4 mg of pyridoxal-5-phosphate monohydrate (5.10.1) in about 800 ml of water (5.1) and dilute with water (5.1) to 1 000 ml.

The solution is stable for 6 months in a closed glass container, if stored at 4 °C $\pm$ 2 °C.

Alternatively:

Dissolve 704 mg $\pm$ 3 mg of disodium phenylphosphate (5.10.2) in about 800 ml of water (5.1), acidify with sulfuric acid II (5.2.2) to pH $\approx$ 2 and dilute to 1 000 ml with water (5.1).

The solution is stable for 3 months if stored in the dark at 4 °C $\pm$ 2 °C.

5.22.5 Organophosphorus solution I, to check UV digestion efficiency, $\rho = 0{,}5$ mg/l P, for the total-P working range II (0,10 mg/l to 1,00 mg/l P).

Dilute 0,5 ml of solution 5.22.4 and 100 µl of sulfuric acid (II) (5.2.2) to 100 ml with water (5.1).

The solution is stable for 1 month if stored at 4 °C ± 2 °C.

5.22.6 Organophosphorus solution II, to check UV digestion efficiency, $\rho = 5{,}00$ mg/l P, for the total-P working range I (1,00 mg/l to 10,0 mg/l P).

Dilute 5 ml of solution 5.22.4 and 100 µl of sulfuric acid (II) (5.2.2) to 100 ml with water (5.1).

The solution is stable for 1 month if stored at 4 °C ± 2 °C.

5.23 Rinsing solution.

Dissolve 65 g of sodium hydroxide, NaOH, and 6 g of tetrasodium ethylenedinitrilotetraacetic acid, Na_4-EDTA, $C_{10}H_{12}O_8N_2Na_4$, in 1 000 ml of water (5.1).

This solution is stable for 1 month if stored at 4 °C ± 2 °C.

6 Apparatus

6.1 Continuous-flow analysis (CFA)

The system generally consists of the following components (see Figures A.1 and A.2)

6.1.1 Sampler or other device for reproducible sample introduction.

For the determination of total-P, consider using a device to mix the sample just before sampling.

6.1.2 Reagent containers.

6.1.3 Peristaltic pump with suitable pump tubes inert to the reagents used.

6.1.4 Manifold with reproducible gas bubble introduction, sample and reagent introduction and components of chemically inert materials.

6.1.5 If necessary, **a dialyser** with a cellulose membrane to dilute the sample and eliminate interfering substances (only for orthophosphate).

6.1.6 If necessary, **flow-through thermostats**, e.g. 37 °C to 40 °C (precision: ± 1 °C), 60 °C (precision: ± 2 °C), or 95 °C (precision: ± 1 °C), respectively.

6.1.7 Photometric flow-through detector, wavelength 880 nm ± 10 nm.

6.1.8 Data display unit, such as a recorder, printer or plotter.

NOTE Figures A.1 and A.2 show CFA systems with tubing of 2 mm internal diameter. Other tubing diameters (e.g. 1 mm) can be used as long as the flowrates are in the same proportion and the recovery rates in 8.5 are achieved.

6.2 Additional apparatus

6.2.1 Graduated flasks, nominal capacity 100 ml, 200 ml and 1 000 ml.

6.2.2 Pipettes, nominal capacity 1 ml, 2 ml, 5 ml, 10 ml, 20 ml and 25 ml.

6.2.3 Beakers, nominal capacity 25 ml, 100 ml and 1 000 ml.

6.2.4 Disposable membrane filter assembly, with membrane filters of pore size 0,45 µm.

For samples with a large particulate load, the disposable filters may incorporate a glass fibre pre-filter.

6.2.5 pH meter.

6.3 Additional apparatus for the determination of total phosphorus after integral digestion

6.3.1 Homogenizer.

6.3.2 Apparatus integrated in the CFA system (6.1):

6.3.2.1 UV digestion unit, e.g. with ozone-producing lamp and reaction coil of quartz glass (see Figure A.2).

NOTE In-line digestors with a power of 25 W are commercially available (see e.g. Figure A.2).

6.3.2.2 Thermostat for temperature control of the hydrolysis at 95 °C ± 1 °C.

7 Sampling and sample preparation

Carry out sampling according to ISO 5667-1, ISO 5667-2 and ISO 5667-3. Prior to use, rinse with water (5.1) all containers which will come into contact with the sample.

For samples with low concentrations (e.g. $\leqslant$ 0,1 mg/l orthophosphate-P), use glass containers. For samples with higher concentrations (e.g. $>$ 0,1 mg/l orthophosphate-P or total-P), plastics bottles (e.g. made from high density polyethene) are also acceptable.

If filtering is required (in the case of particles of diameter $>$ 0,1 mm), samples for the determination of orthophosphate should be filtered through a membrane filter (0,45 µm) immediately after sampling and stored at 4 °C ± 2 °C. The filtration reduces biological reactions, and avoids interferences by sulfide and clogging of the analyser tubing (in case of solids of diameter larger than 100 µm). Maximum preservation time: 24 h.

Samples for the determination of total-P shall be preserved either by freezing (−18 °C) or by adding sulfuric acid to a value of pH $<$ 2 immediately after sampling. Maximum preservation time: 1 month. Total phosphorus samples containing particles of diameter larger than 100 µm shall be homogenized (6.3.1).

8 Procedure

8.1 Preparation for analysis

Set up the flow analyser for the desired procedure orthophosphate-P or total-P: see Figures A.1 and A.2.

Pump the reagents for up to 10 min (for total-P: up to 30 min) and adjust the baseline to zero.

The analyser is ready as soon as the baseline is stable. Proceed according to steps 8.2 to 8.5.

8.2 Instrument performance check

In the analytical system, prepared according to 8.1, a calibration solution (5.21) with a phosphate-P concentration of 0,05 mg/l shall exhibit an absorbance per centimetre in Working range II (0,01 mg/l to 0,10 mg/l) of at least 0,015 cm^{-1}. Otherwise the flow system is not suitable, and it shall be replaced by a system which fulfills this requirement.

If the photometric detector (6.1.7) does not allow any absorbance readings, the absorbance may then be determined by comparing with an external absorbance measuring photometer. In this case, a sufficient quantity of the reaction mixture (containing the sample and the appropriate reagent solutions, see Clause 5) should be prepared manually and measured in the external photometer.

A calibration solution (5.21) with a phosphate-P concentration of 0,01 mg/l shall exhibit a signal-to-noise ratio of at least 3:1.

8.3 Reagent blank check

Wait for a stable baseline.

Pump water (5.1) through all tubes. Record the change in absorbance.

If the absorbance per centimetre (see 8.2) is reduced by more than 0,01 cm^{-1}, the reagents or the water (5.1) may possibly be contaminated, and suitable measures to eliminate the interference shall be undertaken before starting the analysis.

Pump all the reagent solutions again (8.1).

8.4 Calibration

Select the desired range and the appropriate calibration solutions (5.21), at least five, equally distributed over the working range. Carry out a separate calibration for each working range.

Before starting the analysis, set the baseline as recommended by the instrument manufacturer, or as appropriate.

Obtain the measured values corresponding to the calibration solutions applied.

Calibrate by sequentially applying the calibration solutions and reagent blanks.

Determine the calibration curve in accordance with ISO 8466-1.

The analysis conditions for standards and samples are identical (8.6). The output signal is proportional to the phosphate-P concentration, or the total-P concentration, respectively. Use the following Equation (1):

$$y = b \cdot \rho + a \tag{1}$$

where

y is the measured value, in system-related units;

b is the calibration-curve slope, in system-related units $\times$ litres per milligram;

ρ is the mass concentration of orthophosphate-P or total P, in milligrams per litre;

a is the calibration-curve intercept, in system-related units.

8.5 Check of UV digestion and hydrolysis for total P determination (see Figure A.2)

Establish a stable baseline.

Potassium pyrophosphate solution I or II (5.22.2, 5.22.3) and organophosphorus solution I or II (5.22.5, 5.22.6) at a concentration of 50 % of the selected working ranges I or II shall show a recovery rate of at least 90 %.

The recovery rate depends on the manufacturer's equipment. If these criteria are not met, replace it by a system which fulfills these requirements.

8.6 Measurement

Analyse samples, prepared according to Clause 7, in the same way as the calibration solutions (5.21).

If the sample concentration is higher than the selected working range, analyse in a different range or dilute prior to analysis.

After each set of sample measurements, at least after every 20 measurements, check the system calibration using calibration solutions in the lower and the upper third of the working range (8.4). If necessary recalibrate the system.

8.7 Closing down the system

To remove any precipitates, close down the flow system as follows.

At the end of a run, rinse the system for about 5 min with the rinsing solution (5.23), and then for about 5 min with water (5.1).

9 Calculation of results

Calculate the mass concentration of the samples using Equation (2):

$$\rho = (y - a) / b \qquad (2)$$

where the symbols are as defined in 8.4.

Calculate sample concentrations according to the calibration range they fall into. Do not extrapolate a calibration curve.

10 Expression of results

Report results to not more than 2 significant figures.

EXAMPLES

Orthophosphate-P:	$2{,}7 \times 10^{-2}$ mg/l
Orthophosphate-P:	0,42 mg/l
Total-P:	0,69 mg/l
Total-P:	2,9 mg/l

11 Test report

The test report shall refer to this part of ISO 15681 and contain at least the following information:

a) identification of the sample;

b) analysis procedure used;

c) sample preparation, if applicable;

d) description of the analyser type or flow analysis conditions used;

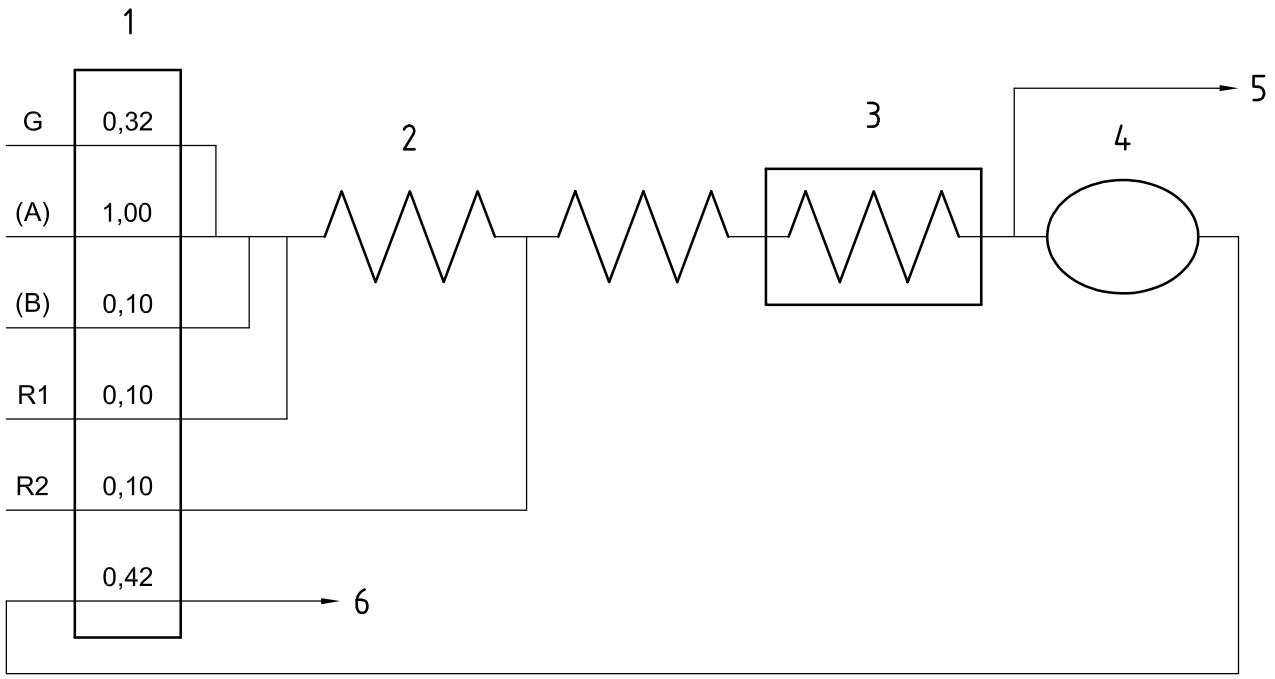
e) results, in accordance with Clause 10;

f) any deviation from this part of ISO 15681 or any circumstances which may affect the result.

Annex A
(informative)

Examples of a CFA system

Figures A.1 and A.2 give examples of a CFA system (see 6.1).



Key

1 pump, flowrates in ml/min
2 reaction coil, $l = 30$ cm, $\varnothing = 2$ mm
3 thermostat coil 37 °C to 40 °C (precision: ± 1 °C), $l = 120$ cm, $\varnothing = 2$ mm
4 detector, wavelength = 880 nm
5 waste
6 debubbled waste

G air: flowrate 0,32 ml/min
R1 antimony tartrate molybdate reagent I (5.14.1): flowrate 0,10 ml/min
R2 ascorbic acid solution I (5.15): flowrate 0,10 ml/min

For orthophosphate-P:

Working range II (0,01 mg/l to 0,10 mg/l P):

(A) sample: flowrate 1,00 ml/min
(B) surfactant solution II (5.11.2): flowrate 0,10 ml/min

Working range I (0,10 mg/l to 1,00 mg/l P):

(A) surfactant solution I (5.11.1): flowrate 1,00 ml/min
(B) sample: flowrate 0,10 ml/min

For total-P (obtained by manual digestion):

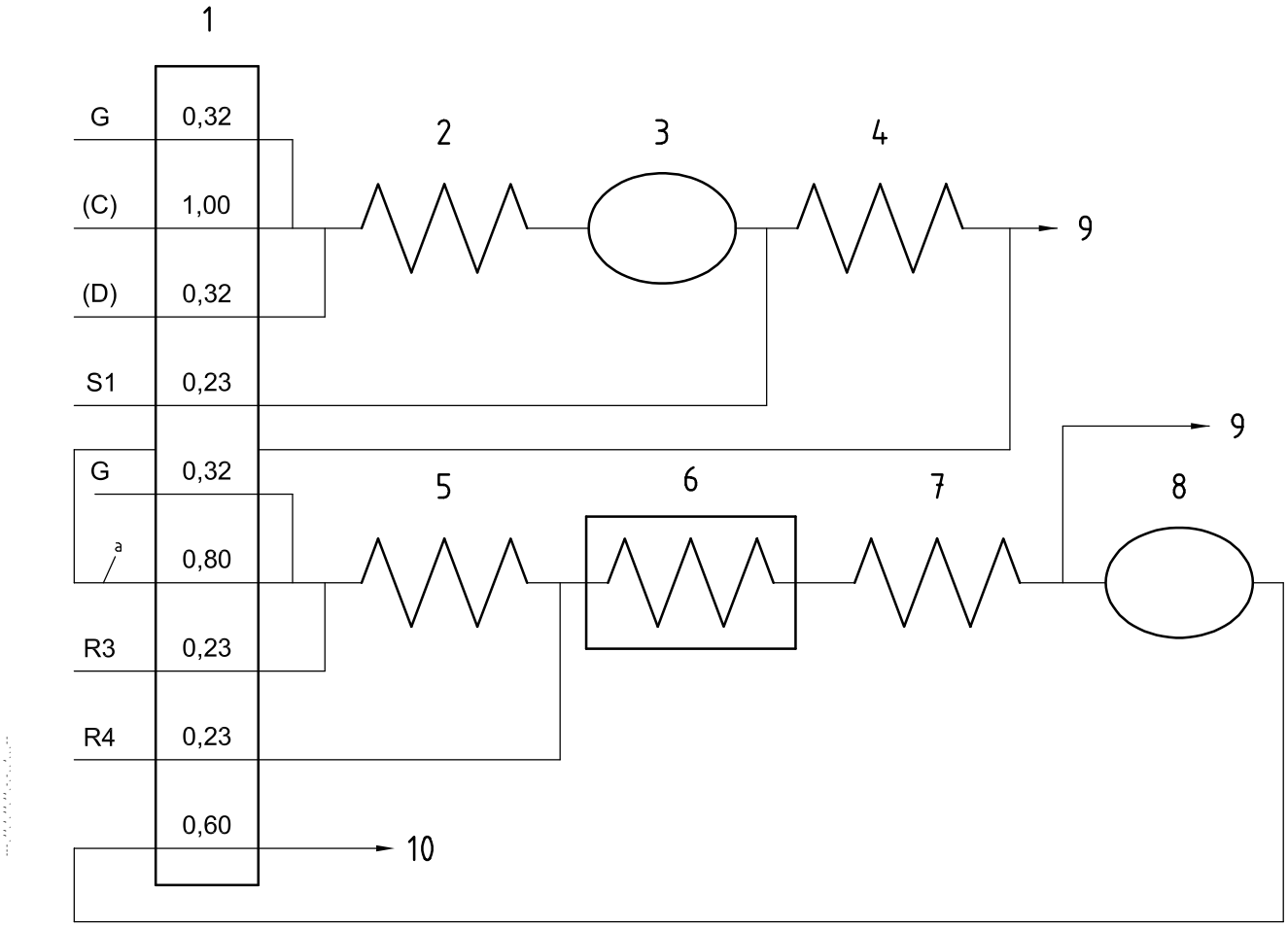
Working range II (0,10 mg/l to 1,00 mg/l P):

(A) surfactant solution I (5.11.1): flowrate 1,00 ml/min
(B) sample: flowrate 0,10 ml/min

Working range I (1,00 mg/l to 10,0 mg/l P):

(A) surfactant solution I (5.11.1): flowrate 1,00 ml/min
(B) sample, diluted 1:10 (offline or online): flowrate 0,10 ml/min

Figure A.1 — Example of a CFA system (6.1) for determination of orthophosphate-P and total-P (obtained by manual digestion) in all concentration ranges



Key

1 pump, flowrates in ml/min
2 reaction coil, $l = 30$ cm, $\varnothing = 2$ mm
3 UV digestor; e.g. with ozone-producing lamp and reaction coil of quartz glass, power of the UV lamp = 25 W, reaction path: $l = 500$ cm, $\varnothing = 2$ mm;
4 reaction coil, $l = 30$ cm, $\varnothing = 2$ mm
5 reaction coil, $l = 30$ cm, $\varnothing = 2$ mm
6 thermostat coil, temperature = 95 °C ± 1 °C, reaction path: $l = 200$ cm, $\varnothing = 2$ mm
7 reaction coil, $l = 120$ cm, $\varnothing = 2$ mm
8 detector, wavelength = 880 nm
9 waste
10 debubbled waste

G air: flowrate 0,32 ml/min
R3 antimony tartrate molybdate reagent II (5.14.2): flowrate 0,23 ml/min
R4 ascorbic acid solution II (5.16): flowrate 0,23 ml/min
S1 surfactant solution II (5.11.2): flowrate 0,23 ml/min

For working range II (0,10 mg/l to 1,00 mg/l P):

(C) sample: flowrate 1,00 ml/min
(D) digestion reagent I (5.17.1): flowrate 0,32 ml/min

For working range I (1,00 mg/l to 10,0 mg/l P):

(C) digestion reagent II (5.17.2): flowrate 1,00 ml/min
(D) sample: flowrate 0,32 ml/min

[a] Resample

Figure A.2 — Example of a CFA system (6.1) for determination of total-P with integrated UV digestion in all concentration ranges

Annex B
(informative)

Precision and accuracy

The statistical data in Tables B.1 and B.2 were obtained from an interlaboratory trial carried out in May 2000 by DIN.

Table B.1 — Statistical data for the determination of orthophosphate-P by CFA
in accordance with ISO 5725-2

Sample	Matrix	l	n	o %	$\bar{x}$ µg/l	s_R µg/l	CV_R %	s_r µg/l	CV_r %
P-1	Drinking water	17	72	0	77,2	12,1	15,7	1,32	1,71
P-2	Surface water	17	51	25	450	33,2	7,38	3,91	0,869
P-3	Waste water	17	60	11,8	526	74,6	14,2	6,15	1,17
P-4	Surface water	16	64	0	280	45,3	16,2	6,99	2,50

Table B.2 — Statistical data for the determination of total-P by CFA
in accordance with ISO 5725-2

Sample	Matrix	l	n	o %	x_{corr} µg/l	$\bar{x}$ µg/l	RR %	s_R µg/l	CV_R %	s_r µg/l	CV_r %
P-1	Drinking water	16	64	0	275	249	91	27,9	11,2	6,31	2,53
P-2	Surface water	16	60	6,25	500	488	98	34,8	7,13	8,27	1,69
P-3	Waste water	16	60	6,25	$4{,}36 \times 10^3$	$4{,}22 \times 10^3$	97	572	13,6	65,4	1,55
P-4	Surface water	16	56	12,5	$3{,}12 \times 10^3$	$3{,}15 \times 10^3$	101	169	5,37	29,0	0,921

Key to Tables B.1 and B.2:

l is the number of laboratory data sets received (including outliers);

n is the number of outlier-free individual analytical values;

o is the relative portion of outliers;

x_{corr} is the correct value of the concentration by convention;

$\bar{x}$ is the total mean of the concentrations, obtained from outlier-free values;

RR is the recovery rate;

s_R is the reproducibility standard deviation;

CV_R is the reproducibility coefficient of variation;

s_r is the repeatability standard deviation;

CV_r is the repeatability coefficient of variation.

The results of the mean values, recovery rates and precision data are equivalent to the corresponding results obtained by the interlaboratory trial on the FIA method (see ISO 15681-1:2003, Annex B).

Annex C
(informative)

Determination of orthophosphate-P and total-P by CFA and tin(II) chloride reduction

The reduction procedures with tin(II) chloride as described in ISO 15681-1 are also applicable for CFA systems. However, this procedure was not validated by the interlaboratory trial (see Annex B).

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