The Testing of Water

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E. Merck, Darmstadt

Preface

The 10th edition of the E. Merck publication "The Testing of Water" is a revision of the 9th edition to take account of changes in nomenclature und additions to our range of rapid tests and ready-to-use test kits for semi-quantitative and quantitative analysis. The methods listed are the same as those in the 9th edition.

In selecting the analytical methods set out herein we have taken into account the literature up to the first half of 1974 as well as our own experiences.

The book does not claim to replace the familiar detailed works on the testing of water. It is intended rather as a handy reference work for the analyst in practice, and sets out to make available to him a number of frequently used methods for the control of waste water, drinking and industrial water, boiler-feed and swimming-pool water.

The parameters to be determined are arranged in alphabetical order. The formulation of the necessary reagent solutions or reagent preparations is given for each determination, followed by a summary of the reagents required, their catalogue numbers and package sizes.

Rapid tests are increasingly being used in the laboratory and, more especially, in field tests where there is no laboratory available. It is often found that semi-quantitative determinations are perfectly adequate in detecting limit values for constituents in drinking water, surface water, industrial and waste water. Quantitative photometric determinations with Spectroquant® test kits are considerably quicker and less laborious than the traditional testing procedures.

Reference is made in this book to the appropriate Aquamerck®/Aquaquant® reagent kits and Merckoquant® test strips. Details of the methods employing these are given in the Merck brochures "Aquamerck® reagent kits for water analysis", "Aquaquant® water analysis system" and "Merckoquant® test strips for detection of various ions and compounds".

The more usual bacteriological methods of water analysis have been compiled in a special brochure.

The following Merck publications can also provide important information on water testing:

Complexometric assay methods with Titriplex®
Organic reagents for trace analysis
Ion exchangers for analytical use
Buffer substances, buffer solutions, buffer Titrisol® concentrates
Titrisol®, Combi-Titrisol®, Titrifix®, volumetric solutions
Standards for atomic absorption spectroscopy, Titrisol® products, reagents
Non-bleeding indicator strips, indicator papers, and liquid indicators for pH measurements.

Contents

I. Analytical Methods for the Testing of Water

Acid-consuming capacity (alkalinity)

Rapid determination possible with Aquamerck® Reagent Kits

Determination of the acid capacity by means of an indicator

The acid-consuming capacity of a water = the number of millimol (mmol) hydrochloric acid consumed on titration of 1000 ml water until the colour change of certain indicators (or until the attainment of certain pH values in the case of electronic measurement).

Determination of the p- and m-value

p-value = number of ml 1 mol/l hydrochloric acid consumed for 1000 ml water on using phenolphthalein as indicator (or to attainment of pH 8.2 in the case of electrometric measurement).

m-value = number of ml 1 mol/l hydrochloric acid consumed for 1000 ml water on using methyl orange as indicator (or to attainment of pH 4.3 in the case of electrometric measurement) less 0.05 meq/l for the m-value of neutral water without buffering constituents.

Interferences and pre-treatment

The titration is not applicable when the water contains substances other than carbonic acid its anions which have a buffering effect in the pH ranges around 4.3 and/or around 8.2. It is also not applicable to coloured waters in which the colour change of the indicator is not clearly detectable. In such cases the titration should be carried out using a glass electrode cell instead of an indicator.

Procedure

To determine the p-value, add 4 drops of phenolphthalein solution to 100 ml water or a smaller volume of the sample made up to 100 ml with deionised water, and titrate with 0.1 mol/l hydrochloric acid from red to colourless. If less than 2 ml of 0.1 mol/l hydrochloric acid is consumed, repeat the titration with 0.02 mol/l hydrochloric acid.

To determine the m-value, add 2 drops of methyl orange solution to 100 ml water or a smaller volume of the sample made up to 100 ml with deionised water, and titrate with 0.1 mol/l hydrochloric acid until the colour of a comparison solution is matched. The colour comparison solution is composed of 100 ml deionised water, 2 drops methyl orange solution and a spatula tip of potassium hydrogen phthalate. If less than 2 ml of 0.1 mol/l hydrochloric acid is consumed, repeat the titration with 0.02 mol/l hydrochloric acid.

Calculation

$$\text{p-value: p [mmol/l]} = \frac{a \times f \times 1000}{c}$$

$$\text{m-value: m [mmol/l]} = \frac{b \times f \times 1000}{c} - 0.05$$

a = ml 0.1 mol/l or 0.02 mol/l hydrochloric acid consumed until colour change of the p-indicator

b = ml 0.1 mol/l or 0.02 mol/l hydrochloric acid consumed until colour change of the m-indicator

c = number of ml water sample used

f = normality of the hydrochloric acid

0.05 = m-value of neutral water without buffering constituents in meq/l

Reporting of results

The values are rounded off to 0.05 mmol/l for less than 10 mmol/l, and to 0.1 mmol/l for 10 mmol/l or higher.

Reagent preparations

Methyl orange solution: Dissolve 0.5 g methyl orange indicator in 100 ml deionised water.

Hydrochloric acid 0.02 mol/l: Dilute 200 ml 0.1 mol/l hydrochloric acid to 1000 ml with deionised water.

Reagents

Cat. No.		Packages
4876	Potassium hydrogen phthalate GR volumetric standard	100 g
1322	Methyl orange (C. I. No. 13025, S. No. 176) indicator	25 g, 100 g
7227	Phenolphthalein solution 1% in ethanol indicator	250 ml, 1 l
9973	Hydrochloric acid 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9060	Hydrochloric acid 0.1 mol/l	1 l, 5 l

Ammonium

Qualitative analysis

Treat 50 ml of the water sample with 0.5 ml potassium sodium tartrate solution and 2 ml Nessler's reagent. In the presence of ammonium ions a yellow to yellowish-brown colouration or yellowish-brown precipitate is produced depending on the concentration. Lower limit of detection: about 0.02 mg/l NH_4^+.

Rapid determination possible with Merckoquant® Test Strips and with Aquamerck®, Aquaquant® and Microquant® Reagent Kits

see Appendix.

Quantitative analysis

The determination should be carried out within three hours of sampling; if this is not possible, it is recommended that the sample be preserved with 1 ml saturated mercury(II) chloride solution per 1000 ml water. In this form the water sample remains unchanged for about 2 weeks.

1. Photometrically at lower concentrations by means of Nessler's reagent

Suitable for the determination of ammonium ions in concentrations between 0.02 and 5.0 mg/l NH_4^+.

Interferences and pre-treatment

Salts and iron ions are kept in solution by addition of potassium sodium tartrate (see Procedure). In the case of waters with over 25° German degrees of hardness, turbidities can develop; in this event 100 ml of the water sample are treated with 1 ml sodium carbonate-sodium hydroxide solution. After settling, the clear water is siphoned or filtered off, and used for the determination, addition of potassium sodium tartrate being dispensed with.

Sulfide ions are removed by addition of zinc sulfate solution and filtering off of the precipitate.

Discolourations and turbidities are eliminated by shaking with freshly precipitated aluminium hydroxide and subsequent filtration, if they cannot be eliminated by filtration alone. Should discolourations and turbidities not be removable by this treatment, the determination is preceded by a distillation as described under Procedure.

For the removal of hydrazine from boiler waters which, like hydroxylamine, urea and amino acids, interferes with the reaction, the water is treated with a little activated charcoal. The mixture is intensively aerated with ammonia-free air for two hours in a washing bottle with sintered glass filter, the charcoal then being filtered or centrifuged off.

If the water sample is discoloured by humic substances, its shade of colour after addition of 2 ml sodium hydroxide solution and 1 ml potassium sodium tartrate solution – but without Nessler's reagent – is determined separately in a 50-ml comparison sample, and taken into account in the calculation. Since filter papers occasionally give off ammonium ions, they are washed before the above-mentioned filtrations with hot, ammonium-free, deionised water.

Procedure

Add 1 ml potassium sodium tartrate solution and 2 ml Nessler's reagent to 50 ml of the water, pre-treated as necessary, or to a smaller volume made up to 50 ml with ammonium-free deionised water. After 5 min reaction time, measure at 425 nm against a blank of ammonium-free deionised water treated in the same manner. The cells should be washed out with ammonium-free deionised water before the measurement. The reference curves are prepared with standard solutions of ammonium chloride treated in the same manner as the water sample.

Very strongly discoloured waters which cannot be decolourised with aluminium hydroxide are to be distilled before the determination. Introduce 500 ml of the water sample or, depending on the ammonium ion concentration, a smaller volume made up to 500 ml with deionised water – neutralised if necessary – into a 1000-ml distillation flask, and add 25 ml of phosphate buffer solution. The end of the vertical condenser of the distillation apparatus should dip into a receiver containing 20–30 ml of ammonium-free deionised water and 5 ml 0.1 mol/l hydrochloric acid. Distill over about 200 ml, and make up the distilliate to 250 ml with ammonium-free deionised water. Use an aliquot portion for the above-mentioned photometric determination.

Calculation

In the calculation the initial volumes of water and the aliquot portion of the distillate which was used for the determination are to be taken into account.

Conversion factors

1 mg NH_4^+ ≙ 0.94 mg NH_3 or 0.78 mg N
1 mg NH_3 ≙ 1.06 mg NH_4^+ or 0.82 mg N
1 mg N ≙ 1.29 mg NH_4^+ or1.22 mg NH_3
1 mmol (meq) ammonium ions ≙ 18.04 mg NH_4^+

Reporting of results

The values are rounded off to 0.01 mg/l NH_4^+ for less than 0.1 mg/l, to 0.02 mg/l NH_4^+ from 0.1–1.0 mg/l, and to 0.1 mg/l NH_4^+ for more than 1.0 mg/l.

Reagent preparations

All the solutions are prepared with ammonium-free deionised water, and all apparatus used washed out with ammonium-free deionised water.

Aluminium hydroxide, freshly prepared: Mix an aqueous solution of Aluminium sulfate cryst. extra pure Ph. Eur. with Ammonia solution min. 25% (0.91) GR, filter off the precipitate, and wash the latter free from sulfate.

Ammonium-free deionised water: Treat deionised water with 1 ml Sulfuric acid 95–97% (about 1.84) GR per 1000 ml, and distill.

Ammonium standard solution: Dissolve 2.966 g Ammonium chloride GR in ammonium-free deionised water to make 1000 ml. 1 ml ≙ 1 mg NH_4^+. The dilutions required for preparation of the reference curve should be freshly prepared from this solution.

Potassium sodium tartrate solution: Dissolve 50 g Potassium sodium tartrate GR in 100 ml ammonium-free deionised water. Add 5 ml Nessler's reagent, and allow to stand for a few days. After settling, or filtration through Asbestos for Gooch crucibles (LAB), fill into a brown bottle for storage.

Sodium carbonate-sodium hydroxide solution: Dissolve 100 g Sodium carbonate 10-hydrate cryst. GR and 50 g Sodium hydroxide pellets GR in 300 ml ammonium-free deionised water with heating.

Sodium hydroxide solution: Dissolve 10 g Sodium hydroxide pellets GR in 90 ml ammonium-free deionised water.

Phosphate buffer solution: Dissolve 14.3 g Potassium dihydrogen phosphate GR and 90.15 g di-Potassium hydrogen phosphate 3-hydrate GR in ammonium-free deionised water to make 1000 ml.

Mercury(II) chloride solution: Add 7–8 g Mercury(II) chloride GR to 100 ml ammonium-free deionised water.

Zinc sulfate solution: Dissolve 15 g Zinc sulfate 7-hydrate GR in 100 ml ammonium-free deionised water.

Reagents

Cat. No.		Packages
2186	Charcoal activated GR	250 g, 1 kg
1102	Aluminium sulfate cryst. extra pure Ph. Eur	1 kg, 5 kg
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l
1145	Ammonium chloride GR	500 g, 1 kg, 5 kg
1560	Asbestos acid washed for Gooch crucibles (LAB)	100 g, 1 kg
4873	Potassium dihydrogen phosphate GR	250 g, 1 kg, 5 kg
5099	di-Potassium hydrogen phosphate 3-hydrate GR	250 g, 1 kg
8087	Potassium sodium tartrate GR	500 g, 1 kg, 5 kg
6391	Sodium carbonate 10-hydrate cryst. GR	1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
9533	Neutralit® Special indicator strips pH 5.0–10.0 nonbleeding graduated in 0.5 pH units	1 pack
9028	Nessler's reagent for ammonium salts	100 ml, 500 ml
4419	Mercury(II) chloride GR	100 g, 250 g, 1 kg
9060	Hydrochloric acid 0.1 mol/l	500 ml, 1 l, 5 l
9973	Hydrochloric acid 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
9542	Special indicator strips pH 4.0–7.0 non-bleeding graduated in 0.2–0.3 pH units	1 pack
8883	Zinc sulfate 7-hydrate GR	500 g, 1 kg, 5 kg

Rapid photometric analysis possible with Spectroquant® Ammonium (indophenol blue method)
see Appendix

2. Titrimetrically at higher concentrations after distillation

Suitable for the determination of ammonium ions in concentrations > 5 mg/l NH_4^+.

Interferences and treatment

Urea splits off ammonia on distillation from strongly alkaline solution. In order to keep the error as small as possible, the distillation is carried out at pH 7.4.

Procedure

Introduce 500 ml of the water sample or, depending on the ammonium ion concentration, a smaller volume made up to 500 ml with deionised water – neutralised if necessary – into a 1000-ml distillation flask, and add 25 ml of phosphate buffer solution. The end of the vertical condenser of the distillation apparatus should dip into a receiver containing about 50 ml boric acid solution. Distill over about 200 ml. Treat the distillate with 3 drops of Mixed indicator 5, and with sulfuric acid 0.025 mol/l until the colour changes from green to reddish-violet. As colour comparison, prepare a blank of 50 ml boric acid solution made up with ammonium-free deionised water to about the same volume as the distillate and treated with 3 drops of Mixed indicator 5.

Calculation

$$\text{mg/l } NH_4^+ = \frac{a \times 0.90 \times 1000}{b}$$

a = ml 0.025 mol/l sulfuric acid consumed
b = ml test water used

1 ml 0.025 mol/l sulfuric acid ≙ 0.90 mg NH_4^+

Reporting the results

The values are rounded off to 0.1 mg/l.

Reagent preparations

All solutions are prepared with ammonium-free deionised water, and all apparatus washed out with ammonium-free deionised water.

Ammonium-free deionised water: Treat deionised water with 1 ml Sulfuric acid 95–97% (about 1.84) GR per 1000 ml, and distill.

Boric acid solution: Dissolve 40 g Boric acid cryst. GR in ammonium-free deionised water to make 1000 ml.

Phosphate buffer solution: Dissolve 14.3 g Potassium dihydrogen phosphate GR and 90.15 g di-Potassium hydrogen phosphate 3-hydrate GR in ammonium-free deionised water to make 1000 ml.

Sulfuric acid 0.025 mol/l: Dilute the contents of one Titrisol ampoule 0.05 mol/l Sulfuric acid concentrated solution for preparation of 1 litre of 0.1 N solution to 2000 ml with ammonium-free deionised water.

Reagents

Cat. Nr.		Packages
165	Boric acid cryst. GR	500 g, 1 kg, 5 kg
4873	Potassium dihydrogen phosphate GR	250 g, 1 kg, 5 kg
5099	di-Potassium hydrogen phosphate GR	250 g, 1 kg
6130	Mixed indicator 5 for ammonia titrations	250 ml
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
9984	Sulfuric acid 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 solution	1 amp.
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
9542	Special indicator strips pH 4.0–7.0 non-bleeding graduated in 0.2–0.3 pH units	1 pack

Arsenic

Qualitative analysis

Marsh test (simplified form)

Treat the test water in a test-tube with zinc, sulfuric acid and a little copper sulfate. Close the test-tube with a cork through which passes a right-angled tube of heavy fusible glass drawn out at the end to a 10-cm long capillary tube. Expel the air from the apparatus completely, and heat the capillary tube with a small flame. In the presence of arsenic (or antimony) a black mirror forms inside the capillary beyond the heated part.

If the hydrogen evolved at the capillary tube is ignited without the latter being heated, it burns in the presence of arsenic (or antimony) with a pale blue flame, and in the process both metals are combusted to oxides which are recognisable from the white smoke.

An externally glazed, cold porcelain dish held in the flame yields deposits of arsenic (or antimony) as black metal. To distinguish between arsenic and antimony the metallic mirror is treated with alkaline hydrogen peroxide solution; arsenic disappears, antimony is unaffected.

Rapid determination possible with Merckoquant® Test Strips

see Appendix

Reagent preparations

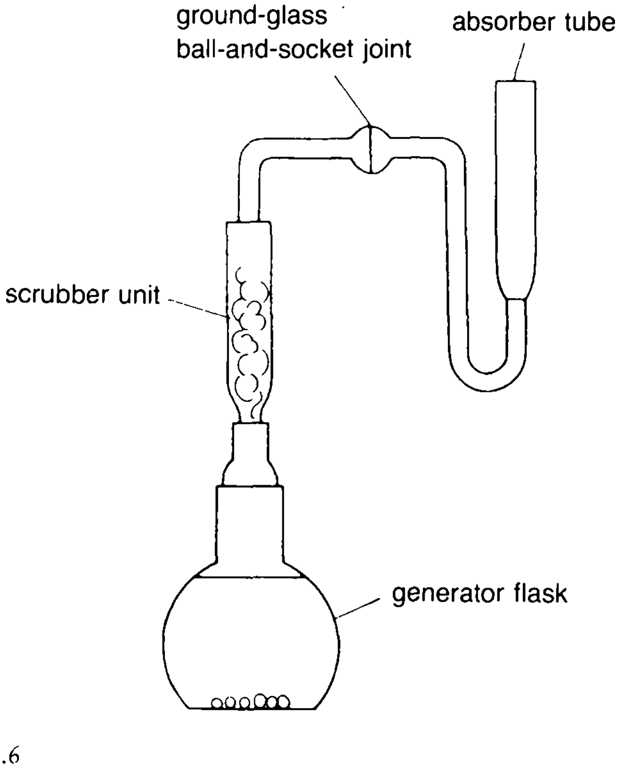
Sodium hydroxide solution: Dissolve 10 g Sodium hydroxide pellets GR in 90 ml deionised water.

Sulfuric acid (about 1.27): Stir one part by volume Sulfuric acid 95–97% (about 1.84) GR carefully into 3 parts by volume deionised water.

Hydrogen peroxide solution, alkaline: Dilute 10 ml Perhydrol 30% H_2O_2 GR with 90 ml deionised water, and make alkaline with sodium hydroxide solution. The solution should be freshly prepared.

Reagents

Cat. No.		Packages
2790	Copper(II) sulfate 5-hydrate GR	250 g, 1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
8780	Zinc granular GR	500 g, 1 kg



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Quantitative analysis

Photometrically by means of silver diethyldithiocarbamate

Suitable for determination of arsenic ions in concentrations from 0.002 to 0.1 mg/l As^{3+}.

Interferences and pre-treatment

Oxidising substances which can prevent a reduction of the arsenic ions to arsine are reduced by means of tin(II) chloride solution before the determination.

Antimony ions interfere in the determination, since they similarly form a red colour complex with silver diethyldithiocarbamate. Up to 1 mg/l Sb can be satisfactorily eliminated by addition of a total of 4.0 ml tin(II) chloride solution.

The possibility of interference from hydrogen sulfide can be excluded by treatment with lead(II) acetate solution (see Procedure). In the case of very high concentrations (more than 200-fold the content of arsenic) low values are obtained despite such treatment. In this case the sample is evaporated to dryness on a water bath with 1 ml nitric acid. The residue is moistened with 2 ml nitric acid, re-evaporated, taken up with 2 mol/l sodium hydroxide, neutralised with 1 mol/l sulfuric acid, and transferred quantitatively to the generator flask of the apparatus.

Procedure

The determination is carried out in an apparatus as illustrated on page 14. First charge the absorber tube with 6.0 l silver diethyldithiocarbamate solution, and the scrubber unit with glass wool impregnated with lead acetate. Then mix 250 ml of the water sample in the generator flask (250 or 500 ml capacity, NS 29) with 20 ml 4 mol/l sulfuric acid, 8 ml potassium iodide solution and 1.3 ml tin(II) chloride solution (in the presence of up to 1 mg/l antimony ions: 4.0 ml), allow to stand for 10 min, add 12 ± 1 g zinc granules (coppered) and immediately connect up the parts of the apparatus.

The arsine formed is driven into the reagent solution by the hydrogen evolved. After exactly 60 min transfer the reagent solution into a 1-cm cell, and measure at 546 nm against a blank of 250 ml deionised water treated in the generator flask in the same manner.

The reference curve is prepared by means of standard solutions of arsenic trioxide or dilutions of Arsenic standard solution Titrisol treated in the same manner as the water sample.

Reporting of results

The values are rounded off to 0.001 mg/l As for less than 0.1 mg/l, and to 0.01 mg/l As for 0.1 mg/l or higher. 1 mmol arsenic ≙ 74.9 mg As.

Reagent preparations

Arsenic standard solution: Dissolve 1.320 g di-Arsenic trioxide resublimed GR volumetric standard (dried over Silica gel with moisture indicator to constant weight) in 12 ml 2 mol/l sodium hydroxide. Neutralise the solution with 1 mol/l sulfuric acid, and dilute with deionised water to 1000 ml. 1 ml ≙ 1 mg As.

Arsenic standard solution: Dilute the contents of one ampoule of Arsenic standard solution Titrisol with double-distilled water to make 1000 ml. 1 ml ≙ 1 mg As.

The dilutions required for preparation of the reference curve should be freshly prepared from the arsenic standard solution.

Lead(II) acetate solution: Dissolve 10 g Lead(II) acetate 3-hydrate GR in 100 ml deionised water.

Glass wool/lead acetate: Impregnate Glass wool (LAB) with the lead acetate solution, and dry at 120° C.

Potassium iodide solution: Dissolve 15 g Potassium iodide neutral GR in 100 ml deionised water. The solution should be stored in a dark bottle.

Sodium hydroxide 2 mol/l: Dilute the contents of one ampoule of 1 mol/l Sodium hydroxide Titrisol concentrated solution for preparation of 1 litre of 1 N solution with deionised water to make 500 ml.

Sulfuric acid 1 mol/l: Dilute the contents of one ampoule of 0.5 mol/l Sulfuric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution with deionised water to make 500 ml.

Sulfuric acid about 4 mol/l: Dilute 222 ml Sulfuric acid 95–97% (about 1.84) GR carefully with deionised water to make 1000 ml.

Silver diethyldithiocarbamate solution: Dissolve 1 g Silver diethyldithiocarbamate GR in 200 ml Pyridine GR. The solution should be stored in a dark bottle.

Zinc granules (coppered): Copper 100 g Zinc granular GR in a solution of copper sulfate (1 g Copper(II) sulfate GR in 100 ml deionised water) until the granules are uniformly black. Then wash with deionised water and dry.

Tin(II) chloride solution: Dissolve 40 g Tin(II) chloride GR in 100 ml Hydrochloric acid min. 25% (about 1.125) GR.

The reagents must be free from arsenic to the extent that the absorbance of the blank is not more than 0.01 greater than that of the silver diethyldithiocarbamate solution.

Reagents

Cat. No.		Packages
9939	Arsenic standard solution Titrisol® 1.000 g ± 0.002 g As (As_2O_3 in water)	1 ampoule
120	di-Arsenic trioxide resublimed GR volumetric standard	100 g
7375	Lead(II) acetate 3-hydrate GR	250 g, 1 kg
4086	Glass wool (LAB)	500 g
5043	Potassium iodide neutral GR	250 g, 1 kg, 2½ kg
1925	Silica gel with moisture indicator (blue gel) (LAB)	1 kg, 5 kg
2790	Copper(II) sulfate 5-hydrate GR	250 g, 1 kg, 5 kg
9136	Sodium hydroxide 2 mol/l	1 l
9956	Sodium hydroxide 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9533	Neutralit® Indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
9728	Pyridine GR	500 ml, 1 l, 2½ l
454	Nitric acid min. 65% (about 1.40) GR	1 l, 2½ l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
9981	Sulfuric acid 0.5 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
1515	Silver diethyldithiocarbamate GR (reagent for arsenic and antimony)	5 g
8780	Zinc granular GR	500 g, 1 kg
7815	Tin(II) chloride GR	100 g, 250 g, 1 kg

Base-consuming capacity (acidity)

Rapid determination possible with Aquamerck® Reagent Kit
see Appendix

Determination of the base-consuming capacity by means of indicators

The base-consuming capacity of a water = the number of milligram equivalents (meq) of sodium hydroxide solution consumed on titration of 1000 ml water until the colour change of certain indicators (or in the case of electrometric measurement to attainment of certain pH values).

Determination of the negative p- and m-values

neg. p-value = number of ml 1 mol/l sodium hydroxide consumed for 1000 ml water on using phenolphthalein as indicator (or in the case of electrometric measurement to attainment of pH 8.2)

neg. m-value = number of ml 1 mol/l sodium hydroxide consumed for 1000 ml water on using methyl orange as indicator (or in the case of electrometric measurement to attainment of pH 4.3)

Interferences and pre-treatment

The titration is not applicable when the water contains substances other than carbonic acid and ions which effect a buffering in the pH ranges about 4.3 and/or 8.2. It is also not applicable to coloured waters when the colour change of the indicator is not clearly detectable. In such cases the titration should be carried out using a glass electrode cell instead of an indicator.

Procedure

To determine the negative p-value, add 4 drops of phenolphthalein solution to 100 ml water or a smaller volume of the sample made up to 100 ml with deionised water, and titrate with 0.1 mol/l sodium hydroxide from colourless to just faintly pink. If less than 2 ml of 0.1 mol/l sodium hydroxide is consumed, repeat the titration with 0.02 mol/l sodium hydroxide.

To determine the negative m-value add 2 drops of methyl orange solution to 100 ml water or a smaller volume of the sample made up to 100 ml with deionised water, and titrate with 0.1 mol/l sodium hydroxide until the colour of a comparison solution is matched. The colour comparison solution is composed of 100 ml deionised water, 2 drops of methyl orange and a spatula tip of potassium hydrogen phthalate. If less than 2 ml of 0.1 mol/l sodium hydroxide is consumed, repeat the titration with 0.02 mol/l sodium hydroxide.

Calculation

$$\text{neg. p-value: } -\text{p [mmol/l]} = \frac{a \times f \times 1000}{c}$$

$$\text{neg. m-value: } -\text{m [mmol/l]} = \frac{b \times f \times 1000}{c}$$

a = ml 0.1 mol/l or 0.02 mol/l sodium hydroxide consumed until colour change of the p-indicator

b = ml 0.1 mol/l or 0.02 mol/l sodium hydroxide consumed until colour change of the m-indicator

c = number of ml water sample used

f = normality of the sodium hydroxide solution

Reporting of results

The values are rounded off to 0.05 mmol/l for less than 10 mmol/l, and to 0.1 mmol/l for 10 mmol/l or higher.

Reagent preparations

Methyl orange solution: Dissolve 0.5 g Methyl orange indicator in 100 ml deionised water.

Reagents

Cat. No.		Packages
4874	Potassium hydrogen phthalate GR	250 g, 1 kg
1322	Methyl orange (C. I. No. 13025, S. Nr. 176) indicator	25 g, 100 g
9959	Sodium hydroxide 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9141	Sodium hydroxide 0.1 mol/l	1 l, 5 l
9142	Sodium hydroxide 0.02 mol/l	500 ml
7227	Phenolphthalein solution 1% in ethanol indicator	250 ml, 1 l

Biochemical oxygen demand (BOD_5)

The biochemical oxygen demand (BOD) gives information on the oxygen required by a water for chemical degradation of the organic constituents in association with microorganisms, generally over a period of 5 days (BOD_5), and sometimes also a greater or lesser number of days, at 20° C in the dark. The method is suitable for determination of the BOD_5 in undiluted (Method 1) or diluted (Method 2) water samples in which the oxygen content is still at least 2 mg/l O_2 after the period of consumption.

1. Determination of the BOD_5 without dilution of the water sample

In the case of waters with low BOD_5 (e.g., surface waters such as river water, etc.) the determination can be carried out without dilution when such waters are enriched with additional oxygen.

Interferences and pre-treatment

Strongly acid or strongly alkaline waters are neutralised to pH 7–8.

Active chlorine is bound by addition of an equivalent amount of 0.01 mol/l sodium thiosulfate solution.

Water samples free from or low in microorganisms are inoculated with 0.3 ml sedimented domestic effluent, 2 ml biologically purified waste water or 5–10 ml river water per 1000 ml, depending on the purpose of the determination.

If the water contains substances which consume oxygen without the action of microorganisms (e.g., iron(II) compounds, hydrogen sulfide or sulfur dioxide), and only the biochemical degradation is to be determined, the test water enriched with oxygen is left to stand for two hours before the determination is carried out.

Procedure

Fill a clear-glass bottle with bevelled stopper of about 500-ml capacity to overflowing (to ensure freedom from air-bubbles) with the test water at the sampling site, and closure the bottle. In the laboratory, pre-treat the water if necessary, and pass in oxygen for about 2–3 min from a cylinder via a glass frit or a fine-drawn glass tube to enrich the oxygen content of the water to about 25–30 mg/l O_2. Fill this water into three oxygen determination bottles (clear-glass bottles of 110–130 ml capacity with bevelled glass stoppers and capacities accurately known to 0.1 ml) up to the lip of the bottles and avoiding air bubbles. Closure two of the bottles (B_1 and B_2) immediately, and store for 5 days at 20° C (in a thermostat, incubator, et sim.). Using oxygen determination pipettes, introduce 1.0 ml each of manganese(II) chloride solution and sodium hydroxide solution containing potassium iodide into the third flask, and then proceed as stated under "Determination of dissolved oxygen, Procedure" on page 147. Allow the other two bottles (B_1 and B_2) to stand for 5 days, and subsequently determine the oxygen in the same manner.

Calculation

The oxygen content is calculated from the three determinations by the formula given under "Determination of dissolved oxygen, Calculation" (page 147), 2.0 ml being inserted for b.
A = mg/l O_2 (Bottle A)
B = mg/l O_2 (mean value of Bottles B_1 und B_2)
BOD_5 (mg/l O_2) = A–B

Reporting of results

The values are rounded off to 0.1 mg/l O_2.

Reagents

See "Determination of dissolved oxygen, Reagents" (page 148).

2. Determination of the BOD_5 with dilution of the water sample

Heavily contaminated waters and effluents, i.e., those with a higher biochemical oxygen demand, are so diluted with oxygen-rich "consumed" water that at least 2 mg/l O_2 is still present after the period of consumption.

In the case of a BOD_5 difficult to estimate it is expedient to prepare several graduated dilutions, and use the sample in which about half of the oxygen originally available is consumed.

The COD value can be taken as an indication of the required degree of dilution of the test water: A BOD_5 of about COD/1.40 can be expected in the case of biologically untreated domestic effluents or industrial waste waters which are easily biologically degradable. In the case of biologically treated waters the BOD_5 value is much lower.

Interferences and pre-treatment

Strongly acid or strongly alkaline waters are neutralised to pH 7–8.

Active chlorine is bound by addition of an equivalent amount of 0.01 mol/l sodium thiosulfate.

If the water contains substances which consume oxygen without the action of microorganisms (e.g., iron(II) compounds, hydrogen sulfide or sulfur dioxide), and only the biochemical degradation is to be determined, the undiluted water sample is left to stand for two hours before the determination is carried out.

Water samples free from or low in microorganisms are prepared with dilution water which has been inoculated with 0.3 ml sedimented domestic effluent, 2 ml biologically purified waste water or 5–10 ml river water, preferably outfall water, per 1000 ml, depending on the purpose of the determination. Where it is not possible for technical reasons to adhere to the consumption period of 5 days, it is advisable to freeze the water samples in polyethylene bottles in a deep-freeze, and to prepare them for determination at a time when the desired consumption period can be guaranteed. Should no deep freeze be available, the BOD_n values found after n days can be converted into BOD_5 values, but only with factors obtained with domestic effluent (see Calculation).

Procedure

It is expedient to mix the test water and the dilution water in a 1000-ml graduated cylinder with the aid of a V2A rod of appropriate length fitted at the lower end with a round V2A sieve plate. Mix the dilutions of the water sample by careful up- and down-movement of the rod, avoiding formation of air bubbles. Fill three oxygen determination bottles (clear-glass bottles of 250–300 ml capacity with bevelled stoppers and capacity accurately known to 0.1 ml) in each case with one of the dilutions – graduated where necessary – of the water sample up to the lip, without air bubbles. Using oxygen determination pipettes, introduce into one bottle (A_1) 2.0 ml each of manganese(II) chloride solution and sodium hydroxide solution containing potassium iodide, in that order, and then proceed as stated under "Determination of dissolved oxygen, Procedure" on page 147. Closure the other two bottles (A_2 and A_3) immediately, allow to stand for 5 days at 20° C in the dark (in a thermostat, incubator, et sim.), and subsequently determine the oxygen content.

To determine the BOD_5 of the "consumed" or possibly inoculated dilution water (as blank) fill three oxygen determination bottles (B_1, B_2, B_3) to the lip with such water, avoiding air-bubbles. Then proceed as above.

Calculation

Only those samples are evaluated whose residual oxygen content is at least 2 mg/l O_2 and whose consumption is at least 1 mg/l O_2 without the consumption of the dilution water.

Initially, the oxygen content is calculated from the six determinations (A_1, A_2, A_3 and B_1, B_2, B_3) by the formula given under "Determination of dissolved oxygen, Calculation" (page 147), 4.0 ml being inserted for b.

The mean value is taken in each case for the oxygen contents A_2, A_3 and B_2, B_3. The BOD_5 of the water sample is calculated by the formula:

$$BOD_5\ [\text{mg/l}O_2] = \left[\left(A_1 - \frac{A_2 + A_3}{2}\right) - \left(B_1 - \frac{B_2 + B_3}{2}\right)\right] \times \frac{1000}{V} + \left(B_1 - \frac{B_2 + B_3}{2}\right)$$

V = volume in ml of the test water made up to 1000 ml with the dilution water

In the case of dilutions of the water sample greater than 1 + 99, the BOD_5 is calculated by the following simplified formula:

$$BOD_5\ [\text{mg/l}\ O_2] = \left[\left(A_1 - \frac{A_2 + A_3}{2}\right) - \left(B_1 - \frac{B_2 + B_3}{2}\right)\right] \times \frac{1000}{V}$$

Where the consumption period of 5 days could not be adhered to, the BOD_n value found after n days can be converted into the BOD_5 value by multiplication by the following conversion factors:

Consumption period	2	3	4	5	6	7	8	days
Factor	1.852	1.370	1.136	1.000	0.909	0.854	0.813	

Reporting of results

A BOD_5 of less than 100 mg/l is rounded off to 1 mg/l, of 100–500 mg/l to 5 mg/l, and more than 500 mg/l to 10 mg/l.

Reagent preparations

See "Determination of dissolved oxygen, Reagents" (page 148); also:

Dilution water: To guarantee a constant quality of the dilution water it is advisable to use deionised water (free from copper ions and active chlorine) to which the following four buffer and nutrient salt solutions have been added in the amount of 1 ml each per 1000 ml:

Solution 1:
Dissolve 8.5 g Potassium dihydrogen phosphate GR, 28.5 g di-Potassium hydrogen phosphate 3-hydrate GR, 33.4 g di-Sodium hydrogen phosphate 2-hydrate GR and 1.7 g Ammonium chloride GR in deionised water to make 1000 ml. The pH of the solution should be 7.2.

Solution 2:
Dissolve 22.5 g Magnesium sulfate GR in deionised water to make 1000 ml.

Solution 3:
Dissolve 36.5 g Calcium chloride 2-hydrate cryst. GR in deionised water to make 1000 ml.

Solution 4:
Dissolve 0.25 g Iron(III) chloride GR in deionised water to make 1000 ml.

If the water samples to be diluted are free from or low in microorganisms, add 2 ml biologically purified waste water, 0.3 ml sedimented domestic effluent or 5–10 ml river water per 1000 ml dilution water.

Then aerate the water in the dark at 20°C until it is saturated with oxygen and no longer exhibits a biochemical oxygen demand (consumed dilution water). The residual BOD_5, which may not exceed 1 mg/l, is to be determined as blank value, and taken into account in the calculation.

Reagents

Cat. No.		Packages
1145	Ammonium chloride GR	500 g, 1 kg, 5 kg
2382	Calcium chloride 2-hydrate cryst. GR	500 g, 1 kg, 5 kg
3943	Iron(III) chloride GR	250 g, 500 g, 1 kg
4873	Potassium dihydrogen phosphate GR	250 g, 1 kg, 5 kg
5099	di-Potassium hydrogen phosphate 3-hydrate GR	250 g, 1 kg
5886	Magnesium sulfate GR	500 g, 1 kg, 5 kg
6580	di-Sodium hydrogen phosphate 2-hydrate GR	500 g, 1 kg, 5 kg
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack

Cadmium

Quantitative analysis

Photometrically with dithizone

Suitable for determination of cadmium ions in concentrations from 0.01 to 20 mg/l Cd^{2+}.

Interferences and pre-treatment

The interference of zinc, copper, lead, manganese, chromium, nickel, silver and tin ions may be excluded up to concentrations of a total of 10 mg in the sample volume used by means of appropriate reaction conditions.

Cobalt ions up to 10 mg in the initial volume of water are masked by addition of 1.5 ml dimethylglyoxime solution. Iron(III) ions interfere in concentrations from about 50 mg in the volume of water used.

Multiples of the above-mentioned concentrations of the various interfering factors can be separated by repetition of the extraction (see Procedure). Intensive extraction favours a separation as nearly quantitative as possible.

Organic constituents (corresponding to a potassium permanganate-consuming capacity > 30 mg/l) are eliminated by evaporation and fuming off of the water sample with addition of 5 ml sulfuric acid and 5 ml nitric acid. Higher concentrations of special organic substances in waste waters can lead to low values despite the pre-treatment.

Oxidising constituents are eliminated by addition of hydroxylammonium chloride solution.

Because of the great sensitivity of the method and the ease of adsorption of cadmium onto surfaces a thorough cleaning of the glass apparatus used is necessary. After the normal cleaning the apparatus should be rinsed with nitric acid (1 + 1) and then with double-destilled water.

Procedure

Pipette 50 ml or a smaller volume of the water sample, which should contain between 0.5 and 20 µg Cd^{2+}, into a glass beaker. Undissolved cadmium compounds can be brought into solution by heating for 10 min with 5 ml of 2 mol/l hydrochloric acid. In the case of turbidity, filter the solution. After cooling, add 5 ml potassium sodium tartrate solution, 1 drop of methyl orange solution, and then 2 mol/l sodium hydroxide dropwise until the colour changes from red to yellowish-orange. Transfer the solution quantitatively to a 100-ml separating funnel, treat with 5 ml sodium hydroxide-potassium cyanide solution a, 2 ml hydroxylammonium chloride solution and 15 ml dithizone solution a in that order, mixing thoroughly on each addition. Shake for 1 minute, allow the layers to separate, and transfer the solvent phase to a second 100-ml separating funnel containing 25 ml cold tartaric acid solution. Pipette 10 ml chloroform into the first separating funnel. Shake again for 1 minute, allow the chloroform to separate, and transfer it to the second separating funnel, taking care that none of the strongly alkaline aqueous phase is entrained. Shake the second separating funnel for 2 min. Drain off the chloroform phase and discard. Add 5 ml chloroform, shake for 1 min again, and once more discard the chloroform phase after it separates out.

If a further extraction should be necessary to remove higher concentrations of interfering factors, treat the tartaric acid phase once again with 5 ml potassium sodium tartrate solution, 5 ml sodium hydroxide-potassium cyanide solution a, 2 ml hydroxylammonium chloride solution and 15 ml dithizone solution a, and proceed as described above.

To the cold tartaric acid solution add 1 drop hydroxylammonium chloride solution, 15 ml dithizone solution b and 5 ml sodium hydroxide-potassium cyanide solution b in that order. Shake for 1 min, allow the layers to separate, and filter the chloroform phase through a pledget of cotton wool into a closable vessel or directly into the cell. Measure at 530 nm against a blank treated in the same manner and consisting of the same volume of double-distilled water as was added to the water sample.

The reference curve is prepared from standard solutions of cadmium metal or dilution solutions from cadmium standard solution Titrisol treated in the same manner as the water sample.

Calculation

The cadmium content of the sample is calculated in mg/l Cd^{2+} from the volume of water used and the amount of cadmium given by the reference curve.
1 mmol cadmium ions ≙ 112.4 mg Cd^{2+}
1 mg Cd^{2+} ≙ 1.142 mg CdO

Reporting of results

The values are rounded off to 0.01 mg/l for less than 1 mg/l, to 0.1 mg/l from 1 to 10 mg/l, and to 1 mg/l for more than 10 mg/l.

Reagent preparations

Cadmium standard solution: Dissolve 1.000 g Cadmium powder GR in a mixture of 20 ml double-distilled water and 5 ml Hydrochloric acid fuming min. 37% (about 1.19) GR with warming. Transfer the solution quantitatively into a 1000-ml volumetric flask, and make up to the mark with double-distilled water. 1 ml ≙ 1 mg Cd^{2+}.

Cadmium standard solution: Dilute the contents of one ampoule of Cadmium standard solution Titrisol to 1000 ml with double-distilled water. 1 ml ≙ 1 mg Cd^{2+}.

Pipette 10 ml of the cadmium standard solution into a 1000-ml volumetric flask, treat with 10 ml Hydrochloric acid fuming min. 37% (about 1.19) GR, and make up to the mark with double-distilled water. 1 ml ≙ 10 µg Cd^{2+}.

Pipette 100 ml of the diluted cadmium standard solution into a 1000-ml volumetric flask, and make up to the mark with double-distilled water. 1 ml ≙ 1 µg Cd^{2+}. This cadmium solution is used to prepare the reference curve.

The dilution solutions are to be freshly prepared before use in each case.

All the cadmium solutions should be stored in polyethylene bottles.

Dimethylglyoxime solution: Dissolve 3.6 g Dimethylglyoxime disodium salt GR in 100 ml double-distilled water.

Dithizone solution a: Dissolve 50 mg Dithizone (diphenylthiocarbazone) GR in 500 ml Chloroform GR (for determinations with dithizone). Store the solution in brown bottles in a refrigerator after superimposing a layer of 0.05 mol/l sulfuric acid. The solution is stable for about 1 week.

Dithizone solution b: Dilute 50 ml dithizone solution a in a volumetric flask to 500 ml with Chloroform GR (for determinations with dithizone) and store as for solution a.

Hydroxylammonium chloride solution: Dissolve 250 g Hydroxylammonium chloride GR in 850 ml double-distilled water.

Potassium sodium tartrate solution: Dissolve 250 g Potassium sodium tartrate GR in 1000 ml double-distilled water.

Sodium hydroxide 2 mol/l: Dilute the contents of one ampoule of 1 mol/l Sodium hydroxide Titrisol concentrated solution for preparation of 1 litre of 1 N solution with double-distilled water to make 500 ml.

Sodium hydroxide-potassium cyanide solution a: Dissolve 400 g Sodium hydroxide pellets GR and 10 g Potassium cyanide GR in 800 ml double-distilled water.

Sodium hydroxide-potassium cyanide solution a: Dissolve 400 g Sodium hydroxide pellets GR and 0.5 g Potassium cyanide GR in 800 ml double-distilled water.

Nitric acid 1 + 1: Mix 500 ml Nitric acid min. 65% (about 1.40) GR with 500 ml double-distilled water.

Hydrochloric acid 2 mol/l: Dilute the contents of one ampoule of 1 mol/l Hydrochloric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution with double-distilled water to make 500 ml.

Tartaric acid solution: Dissolve 20 g L(+)Tartaric acid GR in 1000 ml double-distilled water. Since the solution must be cold in use, store in a refrigerator.

Reagents

Cat. No.		Packages
2000	Cadmium powder GR	100 g
9960	Cadmium standard solution Titrisol® 1.000 g ± 0.002 g Cd ($CdCl_2$ in water)	1 amp.
2442	Chloroform GR (for determinations with dithizone)	1 l, 2½ l
3061	Dimethylglyoxime disodium salt GR	100 g, 500 g
3092	Dithizone (diphenylthiocarbazone) GR	5 g, 25 g
4616	Hydroxylammonium chloride GR	100 g, 250 g, 1 kg
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
8087	Potassium sodium tartrate GR	500 g, 1 kg
1323	Methyl orange solution 0.1% indicator	250 ml, 1 l
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
9956	Sodium hydroxide 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9136	Sodium hydroxide 2 mol/l	1 l

456	Nitric acid min. 65% (about 1.40) tested by the dithizone method GR	1 l, 2½ l
317	Hydrochloric acid fuming min. 37% (about 1.19) GR	1 l, 2½ l
9970	Hydrochloric acid 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
9984	Sulfuric acid 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9074	Sulfuric acid 0.05 mol/l	1 l, 5 l
804	L(+)Tartaric acid GR	250 g, 1 kg, 5 kg

Calcium

Qualitative analysis

Acidify the water to be tested with acetic acid (1.02), and treat with a few drops of cold, saturated ammonium oxalate solution. In the presence of higher concentrations of calcium ions a fine white precipitate of calcium oxalate is produced immediately in the cold, and at lower concentrations after warming or on standing for longer periods. The precipitate is soluble in strong acids.

Reagent preparation

Ammonium oxalate solution, cold saturated: Dissolve 5 g Ammonium oxalate GR in 100 ml deionised water.

Acetic acid (1.02): Dilute 120 ml Acetic acid glacial min. 96% (about 1.06) GR with deionised water to make 1000 ml.

Reagents

Cat. No.		Packages
1192	Ammonium oxalate GR	250 g, 1 kg
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l

Rapid determination possible with Merckoquant® Test Strips and Aquamerck® Reagent Kit

see Appendix

Quantitative analysis

Titrimetrically by means of Titriplex® III solution with calconcarboxylic acid as indicator

Interferences and pre-treatment

The determination permits titration of calcium ions even in the presence of large amounts of magnesium ions. Barium and strontium ions are co-titrated.

Lead and zinc ions are masked by 2,3-dimercapto-1-propanol.

Other heavy metals may be masked by potassium cyanide.

Iron and manganese ions can be masked up to a total of about 5 mg/l by addition of triethanolamine. Higher concentrations interfere in the titration as a result of the colour of their complex compounds.

Procedure

Add sufficient potassium hydroxide solution to 100 ml of the water sample or a smaller volume made up to 100 ml with deionised water, which should not contain more than 50 mg calcium ions, to bring the pH of the mixture to about 12 and to precipitate any magnesium ions present quantitatively. Add 5–10 drops calconcarboxylic acid solution or 0.2–0.4 g calconcarboxylic acid triturate, and titrate under vigorous stirring (advisably with a magnetic stirrer) with 0.1 mol/l Titriplex III solution until the colour changes from wine-red to pure blue.

Calculation

1 ml 0.1 mol/l Titriplex III solution ≙ 4.008 mg Ca^2 ≙ 5.608 mg CaO

$$\text{mg/l } Ca^{2+} = \frac{a \times 4.008 \times 1000}{b}$$

a = ml of 0.1 mol/l Titriplex III solution consumed
b = ml of test water used
0.5 mol/l calcium ions ≙ 20.04 mg Ca^{2+}

Reporting of results

The values are rounded off to 0.1 mg/l

Reagent preparations

Calconcarboxylic acid solution: Dissolve 0.4 g Calconcarboxylic acid metal (pM) indicator in Methanol GR to make 100 ml. The solution is only stable for a limited period.

Calconcarboxylic acid triturate: Mix 1 g Calconcarboxylic acid metal (pM) indicator with 99 g Sodium sulfate anhydrous GR, and triturate.

Potassium hydroxide solution: Dissolve 25 g Potassium hydroxide pellets GR in 100 ml deionised water.

Reagents

Cat. No.		Packages
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
4595	Calconcarboxylic acid metal (pM) indicator	5 g, 25 g
3409	2,3-Dimercapto-1-propanol for complexometric determinations (LAB)	5 ml, 25 ml
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
5033	Potassium hydroxide pellets GR	500 g, 1 kg, 5 kg
6009	Methanol GR	1 l, 2½ l
6649	Sodium sulfate anhydrous GR	500 g, 1 kg, 5 kg
8431	Titriplex® III solution 0.1 mol/l metal (pM) indicator	500 ml, 1 l
9992	Titriplex® III solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 M solution	1 amp.
8379	Triethanolamine GR	250 ml, 1 l

Quantitative analysis of calcium and magnesium ions simultaneously

1. Titrimetrically by means of Titriplex® III solution, calconcarboxylic acid and Indicator buffer tablets

Interferences and pre-treatment

Any interfering factors present are excluded as described under "Calcium" and "Magnesium".

Procedure

Treat 100 ml of the water sample, neutralised where necessary, with 2 ml sodium

hydroxide solution and 5–10 drops of calconcarboxylic acid solution, and titrate under vigorous stirring (advisably with a magnetic stirrer) with Titriplex III solution until the colour changes from wine-red to pure blue.
The calcium ion content is calculated from the titration result (a).
Add 1 ml Perhydrol to the titrated solution, and heat on a steam bath until colourless. Then add hydrochloric acid until the magnesium hydroxide precipitate is just dissolved. Dissolve an Indicator buffer tablet in the solution, add 1–2 ml ammonia solution, and titrate with 0.1 mol/l Titriplex III solution until the colour changes from red to green.
The magnesium ion content is calculated from the titration result (b).
Depending on the calcium and magnesium ion content, the titration can also be carried out with a smaller volume of the water sample which has been made up to 100 ml with deionised water, or with 0.01 mol/l Titriplex III solution.

Calculation

a) 1 ml 0.1 mol/l Titriplex III solution $\triangleq$ 4.008 mg Ca^{2+} $\triangleq$ 5.608 mg CaO

$$\text{mg/l } Ca^{2+} = \frac{a \times 4.008 \times 1000}{b}$$

a = ml of 0.1 mol/l Titriplex III solution consumed
b = ml of test water used

b) 1 ml 0.1 mol/l Titriplex III solution $\triangleq$ 2.431 mg Mg^{2+} $\triangleq$ 4.031 mg MgO

$$\text{mg/l } Mg^{2+} = \frac{a \times 2.431 \times 1000}{b}$$

a = ml of 0.1 mol/l Titriplex III solution consumed
b = ml of test water used

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Calconcarboxylic acid solution: Dissolve 0.4 g Calconcarboxylic acid metal (pM) indicator in Methanol GR to make 100 ml. The solution is only stable for a limited period.

Sodium hydroxide solution: Dissolve 15 g Sodium hydroxide pellets GR in 85 ml deionised water.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
4595	Calconcarboxylic acid metal (pM) indicator	5 g, 25 g
8430	Indicator buffer tablets for determination of water hardness with Titriplex® solutions	500 tabl., 1000 tabl.
6009	Methanol GR	1 l, 2½ l
6498	Sodium hydroxide pellets GR	500 g
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
8431	Titriplex® III solution 0.1 mol/l metal (pM) indicator	1 l
9992	Titriplex® III solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 M solution	1 amp.

2. Titrimetrically by means of Titriplex® III solution, murexide and Indicator buffer tablets

Interferences and pre-treatment

Strontium ions are co-titrated, but not barium ions. Iron and manganese ions to a total of about 5 mg/l and titanium ions may be masked by addition of triethanolamine, and other heavy metals (cadmium, cobalt, copper, nickel, platinum, mercury, zinc) by addition of solid potassium cyanide.

Phosphates are removed from the water sample by an anion exchanger.

Larger amounts of magnesium ions occasion a poorer colour change during the titration with murexide; in addition, magnesium hydroxide precipitates out on making the solution alkaline, and brings some calcium with it. The titration should therefore be carried out as rapidly as possible, in order to avoid the separation of calcium hydroxide.

Procedure

Add sufficient sodium hydroxide solution to 100 ml of the water sample or a smaller volume made up to 100 ml with deionised water, which should not contain more than 50 mg each of calcium and magnesium ions, to bring the pH of the mixture to at

least 12. Immediately add 5 drops murexide solution or 0.2–0.4 g (1 spatula tip) of murexide triturate, and titrate with 0.1 mol/l Titriplex III solution until the colour changes from orange to violet.
The calcium ion content is calculated from the titration result (a).
Add 1 ml hydrochloric acid to the solution, and heat on a steam bath until colourless. Treat the still warm solution with ammonia solution (0.99) until the colour change of the methyl orange used as indicator. Dissolve an Indicator buffer tablet in the solution, add 1 ml ammonia solution (0.91), and titrate with 0.1 mol/l Titriplex III solution until the colour changes from red to green.
The magnesium ion content is calculated from the titration result (b).

Calculation

a) *1 ml 0.1 mol/l Titriplex III solution* $\triangleq$ 4.008 mg Ca^{2+} $\triangleq$ 5.608 mg CaO

$$\text{mg/l } Ca^{2+} = \frac{a \times 4.008 \times 1000}{b}$$

a = ml of 0.1 mol/l Titriplex III solution consumed
b = ml of test water used

b) 1 ml 0.1 mol/l Titriplex III solution $\triangleq$ 2.431 mg Mg^{2+} $\triangleq$ 4.031 mg MgO

$$\text{mg/l } Mg^{2+} = \frac{a \times 2.431 \times 1000}{b}$$

a = ml of 0.1 mol/l Titriplex III solution consumed
b = ml of test water used

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Ammonia solution (0.99): Mix 94 ml Ammonia solution min. 25% (0.91) GR with 1000 ml deionised water.
Murexide solution: Suspend about 0.1 g Murexide metal (pM) indicator in a few ml deionised water. Shake well, allow to settle, and decant the clear supernatant solution. The solution should be freshly prepared before use.
Murexide triturate: Finely triturate 0.1 g Murexide metal (pM) indicator with 19.9 g Sodium chloride cryst. GR.

Sodium hydroxide solution: Dissolve 10 g Sodium hydroxide pellets in 90 ml deionised water.

Reagents

Cat. No.		Packages
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
8430	Indicator buffer tablets for determination of water hardness with Titriplex® solutions	500 tabl., 1000 tabl.
5240	Ion exchanger Lewatit® MP 7080 GR 0.1–0.25 mm (60–150 mesh ASTM) weak-base anion exchanger macroporous OH form (® = Registered trade mark of Bayer AG)	100 ml, 500 ml
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
1323	Methyl orange solution 0.1% indicator	250 ml, 1 l
6161	Murexide metal (pM) indicator	5 g, 25 g
6404	Sodium chloride cryst. GR	500 g, 1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
317	Hydrochloric acid fuming min. 37% (about 1.19) GR	1 l, 2½ l
8431	Titriplex® III solution 0.1 mol/l metal (pM) indicator	500 ml, 1 l
9992	Titriplex® III solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 M solution	1 amp.
8379	Triethanolamine GR	250 ml, 1 l

Remarks

Advantages:

Method 1: The colour change with calconcarboxylic acid is more contrastive than with murexide.

Method 2: Murexide is more easily decomposed after the titration than calconcarboxylic acid.

Carbon dioxide

Dissolved carbon dioxide (free carbon dioxide), carbonate and hydrogen carbonate ions

The carbon dioxide dissolved in water and the carbonate anions can only be determined indirectly. Since presentation of the calculations would take up more space than is practicable within the scope of this manual, we refer the reader to, for example, the Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, 3. Auflage, D 8 (The calculation of dissolved carbon dioxide (free carbon dioxide), carbonate and hydrogen carbonate ions), and G 1 (Determination of the sum of the dissolved carbon dioxide). Depending on the given conditions, analytical determination on the one hand of the p- and m-values (of the acid- and base-consuming capacities) and on the other hand of the sum of the contents of dissolved carbon dioxide, carbonate and hydrogen carbonate ions and of the pH value (G 1) is a prerequisite for determination of the individual compounds mentioned.

Chemical oxygen demand (COD)

The chemical oxygen demand gives information on the oxygen required by a water for oxidation of almost all water-soluble organic substances, the exceptions being a number of compounds containing nitrogen and only very slightly soluble hydrocarbons.

Pre-treatment

If the water sample contains coarsely dispersed substances whose COD is also to be determined, it must be homogenised, preferably for about 3 min in a mixer.

If the COD of matter capable of sedimentation is to be disregarded, the test water should be allowed to stand for 2 h in an Imhoff funnel, and the clarified sample then decanted for determination.

If the COD of the dissolved matter is to be determined, the sample should be filtered through a soft plaited filter or – better – a glass-fibre filter.

The apparatus used should be scrupulously clean, and the ground-glass joints in particular free from grease.

Procedure

1. For COD values above about 70 mg/l

Introduce 20.0 ml of the water sample (or an aliquot portion thereof made up to 20.0 ml with deionised water) into a conical flask with ground-glass neck of 300 ml capacity, and add 10.0 ml $^1/_{24}$ mol/l potassium dichromate, 0.4 g mercury(II) sulfate, 40 ml concentrated sulfuric acid containing silver sulfate, and a few glass beads. Heat to gentle, but steady boiling over a low gas flame or electric hot plate and under a reflux condenser. After exactly 10 min boiling, allow to cool briefly, wash 50 ml deionised water through the condenser into the flask, and then cool completely in cold water. Add 2 drops of ferroin solution, and titrate with 0.1 mol/l ammonium iron(II) sulfate until the colour changes from bluish-green to reddish-brown.

Determine a blank with 20.0 ml deionised water under exactly the same conditions.

2. *For COD values below about 70 m/l*

Introduce 50.0 ml of the water sample into a conical flask with ground-glass neck, and add 10.0 ml $^1/_{120}$ mol/l potassium dichromate, 1 g mercury(II) sulfate, 80 ml concentrated sulfuric acid containing silver sulfate, and a few glass beads. Then proceed as described under 1. After cooling of the flask add about 80 ml deionised water through the condenser, and then cool completely. Add 2 drops of ferroin solution, and titrate with 0.025 mol/l ammonium iron(II) sulfate until the colour changes from bluish-green to reddish-brown.

Determine a blank with 50.0 ml deionised water under exactly the same conditions.

3. *Analytical method as used in conjunction with the evaluation formula of the German Abwasserabgabengesetz*

Free the water sample from matter capable of sedimentation, introduce 50.00 ml of the sample (or an aliquot portion thereof made up to 50.0 ml with deionised water) into a 500-ml conical flask with ground-glass neck, and add 25.0 ml $^1/_{24}$ mol/l potassium dichromate solution, 1 g silver sulfate and 2 g mercury(II) sulfate in the order given. Carefully add 75 ml concentrated sulfuric acid portionwise, swirl the mixture well, and boil for 2 h under reflux. Allow to cool for 30 min, and wash the condenser through with about 100 ml deionised water. Dilute the contents of the flask to about 350 ml with deionised water, add 2–3 drops ferroin solution, and titrate with 0.25 mol/l ammonium iron(II) sulfate from bluish-green to reddish-brown.

For each analysis determine a blank with 50.00 ml deionised water under exactly the same conditions.

Calculation

$$\text{COD (mg/l } O_2) = \frac{(a-b) \times c \times f \times 8000}{d}$$

a = ml ammonium iron(II) sulfate solution titrated with the blank

b = ml ammonium iron(II) sulfate solution titrated with the water sample

c = molarity of the ammonium iron(II) sulfate solution (0.1 or 0.025 or 0.25)

f = titre of the 0.1 mol/l or 0.025 mol/l or 0.25 mol/l ammonium iron(II) sulfate solution (see under Reagent preparations) calculated from $\frac{25}{e}$ (Method 1 and 3) or from $\frac{20}{e}$ (Method 2)

d = ml test water used

Reporting of results

The values are rounded down to 1 mg/l or 1 g/m^3 for less than 100 mg/l, and to 5 mg/l or 5 g/m^3 for 100 mg/l or higher.

Reagent preparations

Ammonium iron(II) sulfate 0.1 mol/l: Dissolve 39.2 g Ammonium iron(II) sulfate GR in deionised water, add 20 ml Sulfuric acid 95–97% (about 1.84) GR, cool, and make up to 1000 ml with deionised water.

The titre of this solution must be determined daily before use: Titrate a water sample to the end-point, add 10.0 ml $\frac{1}{24}$ mol/l potassium dichromate with a pipette, and titrate with 0.1 mol/l ammonium iron(II) sulfate to same colour change. The number of ml consumed is inserted for e (see Calculation).

Ammonium iron(II) sulfate 0.025 mol/l: Dilute 250 ml 0.1 mol/l ammonium iron(II) sulfate to 1000 ml with deionised water.

The titre of this solution is determined in accordance with the above instructions, using 10.0 ml $\frac{1}{120}$ mol/l potassium dichromate.

Ammonium iron(II) sulfate 0.25 mol/l: Dissolve 98.0 g Ammonium iron(II) sulfate GR in deionised water, add 20 ml Sulfuric acid 95–97% (about 1.84) GR, cool, and make up to 1000 ml with deionised water.

The titre of this solution must be determined daily before use: Dilute 25.0 ml $\frac{1}{24}$ mol/l potassium dichromate with deionised water to about 250 ml, and add 20 ml concentrated sulfuric acid. After cooling, add 2–3 drops of ferroin solution, and titrate with 0.25 mol/l ammonium iron(II) sulfate until the colour changes from bluish-green to reddish-brown. The number of ml consumed is inserted for e (see Calculation).

Potassium dichromate $\frac{1}{24}$ mol/l: Dissolve 12.26 g Potassium dichromate GR in deionised water, and make up to 1000 ml. Dry the potassium dichromate for 2 h in a drying chamber at 105° C before weighing out.

Potassium dichromate $\frac{1}{120}$ mol/l: Dilute 200 ml $\frac{1}{24}$ mol/l potassium dichromate with deionised water to make 1000 ml.

Aliter, dilute 500 ml $\frac{1}{60}$ mol/l potassium dichromate (from Potassium dichromate solution $\frac{1}{60}$ mol/l Titrisol concentrated solution for preparation of 1 litre of 0.1 N solution) to 1000 ml with deionised water.

Sulfuric acid containing silver sulfate: Dissolve 10 g Silver sulfate GR in 1000 ml Sulfuric acid 95–97% (about 1.84) GR.

Reagents

Art. Nr.		Packages
3792	Ammonium iron(II) sulfate GR	500 g, 1 kg, 5 kg
9193	1/40 Ferroin solution redox indicator	100 ml, 500 ml
4864	Potassium dichromate GR	500 g, 1 kg, 5 kg
9928	Potassium dichromate solution $\frac{1}{60}$ mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
4480	Mercury(II) sulfate GR	50 g
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
1509	Silver sulfate GR	25 g, 100 g

Chloride

Qualitative analysis

In higher concentrations chloride ions form a white precipitate of silver chloride with silver ions – with a bluish-violet tinge in normal light, and in the case of smaller amounts only an opalescence or turbidity develops.

For detection the water sample is acidified with 2 mol/l nitric acid, and treated with a few drops of silver nitrate solution. The precipitate is soluble in ammonia solution and insoluble in nitric acid.

Bromide and iodide ions on the other hand give a yellowish-white precipitate of silver bromide or silver iodide with silver ions. Silver bromide is only slightly soluble in ammonia solution, and silver iodide insoluble.

Reagent preparations

Nitric acid 2 mol/l: Dilute the contents of one ampoule of 1 mol/l Nitric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution with deionised water to make 500 ml.

Silver nitrate solution: Dissolve 5 g Silver nitrate GR in deionised water to make 100 ml.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
9966	Nitric acid 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
1512	Silver nitrate GR	25 g, 250 g, 1 kg

Rapid determination possible with Aquamerck®, Aquaquant® and Microquant® Reagent Kits
see Appendix

Quantitative analysis (Mohr-Winkler laboratory method)

Interferences and pre-treatment

Since bromide and iodine ions can be co-determined, they must where necessary be determined separately and taken into account in the calculation.

Iron ions are removed by shaking with 1 g zinc oxide per 100 ml water and then filtering, to remove the resulting iron oxide hydrates.

In the case of more than 0.25 mg/l manganese, 100 ml of the water sample is shaken with 0.5 g magnesium oxide, and then filtered.

Sulfite and sulfide ions may be removed by dropwise addition of dilute hydrogen peroxide solution.

Free hydrogen sulfide is eliminated by boiling of the water sample.

Organic substances are destroyed by boiling with excess potassium permanganate in alkaline solution. After boiling, a few drops of hydrogen peroxide solution are added, and the solution filtered.

Interfering colouration may be eliminated by shaking with chloride-free, freshly precipitated hydroxide or chloride-free, washed activated charcoal, and filtering.

Procedure

Add 1 ml potassium chromate solution to 100 ml of the test water (neutralised where necessary with sodium carbonate solution or dilute sulfuric acid), and titrate with 0.0282 mol/l silver nitrate until the colour change from yellow to yellowish-brown. If the consumption of 0.0282 mol/l silver nitrate is above 35 ml, repeat the titration with a smaller volume of the water made up to 100 ml with deionised water.

Calculation

1 ml 0.0282 mol/l silver nitrate = 1 mg Cl^-
1 mmol chloride ions = 35.46 mg Cl^-

Reporting of results

The values are rounded off to 1 mg/l.

Reagent preparations

Aluminium hydroxide freshly precipitated: Treat an aqueous solution of Aluminium sulfate cryst. extra pure Ph. Eur. with Ammonia solution min. 25% (0.91) GR. Filter off the precipitate, and wash free from sulfate.

Potassium chromate solution: Dissolve 10 g Potassium chromate GR in 100 ml deionised water.

Potassium permanganate 0.002 mol/l: Dilute 100 ml 0.02 mol/ potassium permanganate with boiled and cooled deionised water to make 1000 ml as required.

Sodium carbonate solution: Dissolve 10 g Sodium carbonate anhydrous GR in deionised water to make 100 ml.

Sulfuric acid, dilute: Carefully mix 20 ml Sulfuric acid 95–97% (about 1.84) GR with 80 ml deionised water.

Silver nitrate solution 0.0282 mol/l: Dilute 282 ml 0.1 mol/l silver nitrate with deionised water to make 1000 ml.

Hydrogen peroxide solution, dilute: Dilute 10 ml Perhydrol GR with deionised water to make 100 ml.

Reagents

Cat. No.		Packages
2186	Charcoal activated GR	250 g, 1 kg
1102	Aluminium sulfate cryst. extra pure Ph. Eur.	1 kg, 5 kg
5432	Ammonia solution min. 25% GR	1 l, 2½ l, 5 l
4952	Potassium chromate GR	250 g, 1 kg
9935	Potassium permanganate solution 0.02 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9122	Potassium permanganate solution 0.02 mol/l adjusted against oxalate	1 l
5865	Magnesium oxide GR	100 g, 500 g
6392	Sodium carbonate anhydrous GR	500 g, 1 kg, 5 kg
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
9990	Silver nitrate solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9081	Silver nitrate solution 0.1 mol/l	1 l
8849	Zinc oxide GR	500 g, 1 kg, 5 kg

Rapid photometric analysis possible with Spectroquant® Chloride
see Appendix

Chlorine

Determination of active and free active chlorine

Chlorine present in a water in the form of elementary chlorine, hypochlorous acid or hypochlorite ions is described as "free active chlorine".

Chlorine present in a water in the form of oxidising, chlorine-substituted compounds is described as "bound active chlorine". The sum of the two types is called "active chlorine".

Qualitative analysis

Add 0.5 g potassium iodide, 5 ml phosphate buffer solution and 5 ml DPD reagent solution to about 100 ml test water. In the presence of chlorine a more or less intense red colour develops, depending on the concentration (for Reagents see under Quantitative Analysis).

Rapid determination possible with Aquamerck® Reagent Kits

see Appendix

Quantitative analysis

1. Titrimetric determination of the "active chlorine" by means of N,N-diethyl-1,4-phenylenediammonium sulfate (DPD)

Suitable for the determination of "active chlorine" in concentrations from 0.1 to 4 mg/l.

Interferences

Copper ions in concentrations above 5 mg/l and iron ions in concentrations above 10 mg/l interfere.

The method is not applicable in the presence of higher-valency manganese oxides.

Procedure

In order to exclude the possibility of a further "chlorine consumption" after sampling, it is advisable to titrate the test water immediately.

Introduce 100 ml of the water sample into a narrow-necked conical flask of about 150-ml capacity by means of a pump-pipette, and add 5 ml DPD reagent solution, 5 ml phosphate buffer solution and 1 g potassium iodide. After 5 min, titrate the solution in a magnetic stirrer with ammonium iron(II) sulfate solution until it becomes colourless or an unchanging faint pink. For this purpose use a microburette with injection tube and nozzle, thereby passing in the ammonium iron(II) sulfate solution directly under the surface of the liquid. If the consumption is above 3 ml, start with a smaller volume of the water which has been made up to 100 ml with double-distilled water.

Carry out each determination at least twice.

Calculation

1 ml ammonium iron(II) sulfate solution ≙ 0.1 mg active chlorine

$$\text{mg/l active chlorine} = \frac{a \times 0.1 \times 1000}{b}$$

a = ml of ammonium iron(II) sulfate solution consumed
b = ml of test water used

Reporting of results

The values are rounded off to 0.01 mg/l for less than 1.0 mg/l, and to 0.1 mg/l for 1.0 mg/l or higher.

2. Titrimetric determination of the "free active chlorine" by means of N,N-diethyl-1,4-phenylenediammonium sulfate (DPD)

Suitable for the determination of "free active chlorine" in concentrations from 0.1 to 4 mg/l.

Interferences

Copper ions in concentrations above 5 mg/l and iron ions in concentrations above 10 mg/l interfere.

The method is not applicable in the presence of higher-valency manganese oxides. In the presence of iodide ions, oxidising chlorine-substituted compounds are codetermined, whereas in the absence of iodide ions only "free active chlorine", i.e., elementary chlorine, hypochlorous acid and hypochlorite ions, react with the N,N-diethyl-1,4-phenylenediammonium sulfate.

Procedure

In order to avoid a further "chlorine consumption" after sampling, the water sample should where possible be tested on the spot, e.g. with Aquamerck®.

Introduce 100 ml of the test water into a narrow-necked conical flask of about 150-ml capacity by means of a pump-pipette, and add 5 ml DPD reagent solution and 5 ml phosphate buffer solution. Insert a magnetic stirrer rod with Teflon coating, and titrate the solution in a magnetic stirrer with ammonium iron(II) sulfate solution until the solution becomes colourless or an unchanging faint pink. For this purpose use a microburette with injection tube and nozzle, thereby passing in the ammonium iron(II) sulfate solution directly under the surface of the liquid. If the consumption is above 3 ml, start with a smaller volume of water which has been made up to 100 ml with double-distilled water.

Carry out each determination at least twice.

Calculation

1 ml ammonium iron(II) sulfate solution ≙ 0.1 mg free active chlorine

$$\text{mg/l free active chlorine} = \frac{a \times 0.1 \times 1000}{b}$$

a = ml of ammonium iron(II) sulfate solution consumed
b = ml of test water used

Reporting of results

The values are rounded off to 0.01 mg/l for less than 1.0 mg/l, and to 0.1 mg/l for 1.0 mg/l or higher.

Reagent preparations

Ammonium iron(II) sulfate solution: Dissolve 1.106 g Ammonium iron(II) sulfate GR in freshly boiled and cooled deionised water. Add 2 ml 1 mol/l sulfuric acid, and make up to 1000 ml with the above-mentioned water.

DPD reagent solution: Dissolve 0.11 g N,N-Diethyl-1,4-phenylenediammonium sulfate GR in deionised water with 2 ml 1 mol/l sulfuric acid and 2.5 ml 0.02 mol/l Titriplex III solution, and make up to 100 ml. Store the solution protected from light in a brown bottle. It is unuseable if a discolouration develops.

Phosphate buffer solution: Dissolve 46 g Potassium dihydrogen phosphate GR and 24 g tri-Sodium phosphate 12-hydrate (LAB) in 1000 ml deionised water.

Sulfuric acid 1 mol/l: Make the contents of one ampoule of 0.5 mol/l Sulfuric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution up to 500 ml with deionised water.

Titriplex III solution 0.02 mol/l: Make 200 ml 0.1 mol/l Titriplex III metal (pM) indicator up to 1000 ml with deionised water.

Reagents

Cat. No.		Packages
3792	Ammonium iron(II) sulfate GR	500 g, 1 kg, 5 kg
3121	N,N-Diethyl-1,4-phenylenediammonium sulfate GR	100 g
4873	Potassium dihydrogen phosphate GR	250 g, 1 kg, 5 kg
5043	Potassium iodide neutral GR	100 g, 250 g, 1 kg, 2½ kg
6578	tri-Sodium phosphate 12-hydrate (LAB)	1 kg , 5 kg
9981	Sulfuric acid 0.5 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9992	Titriplex® solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 M solution	1 amp.
8431	Titriplex® III solution 0.1 mol/l metal (pM) indicator	500 ml, 1 l

Chlorine demand

The chlorine demand, or chlorine-binding capacity, is the amount of chlorine required by a water.

Procedure

Fill a few glass-stoppered brown bottles with 1000 ml each of the test water, treat rapidly with increasing amounts of 0.1% chlorine water, and shake well.

The chlorine water may be added in, for example, the following series:

1 ml/l ≙ 1 mg/l Cl_2; 2 ml/l ≙ 2 mg/l Cl_2; 3 ml/l ≙ 3 mg/l Cl_2 etc.

10 min after addition of the chlorine water, introduce 1 g potassium iodide and 3 drops of starch solution into each bottle. Then shake again, and after a further 10 min titrate with 0.01 mol/l sodium thiosulfate in a clear glass vessel until colourless.

Calculation

The titration result is evaluated from the bottle which exhibits an excess of chlorine equivalent to less than 1 ml 0.01 mol/l sodium thiosulfate. This amount of sodium thiosulfate is converted into mg chlorine/l and subtracted from the amount of chlorine added.

1 ml 0.01 mol/l sodium thiosulfate ≙ 0.355 mg Cl_2

Reporting of results

The values are rounded off to 0.1 mg/l Cl_2.

Reagent preparations

Chlorine water (0.1%): Prepare chlorine water by passing chlorine into deionised water, analyse, and dilute accordingly to 0.1% Cl_2 with deionised water.

Determine the chlorine content in accordance with Determination of free active chlorine on page 47.

Sodium thiosulfate 0.01 mol/l: Dilute 100 ml 0.1 mol/l Sodium thiosulfate solution to 1000 ml with boiled and cooled deionised water as required.

Starch solution: Dissolve 0.2 g Starch soluble GR in 100 ml deionised water.

Reagents

Cat. No.		Packages
823235	Chlorine	0.44 l
823236	Chlorine	5.0 l
5043	Potassium iodide GR	100 g, 250 g, 1 kg, 2½ kg
9950	*Sodium thiosulfate solution 0.1 mol/l Titrisol® concentrated* solution for preparation of 1 litre of 0.1 N solution	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	1 l
1252	Starch soluble GR	100 g, 250 g, 1 kg

Chlorine consumption

Procedure

Treat 1000 ml of the test water in a brown glass-stoppered bottle with an amount of chlorine water corresponding to the chlorine demand and an additional 3 ml of chlorine water. Then shake, and store the bottle as near as possible to 22° C (preferably in an incubator). After 30 min, add 1 g potassium iodide and 3 drops of starch solution, and shake again. After a further 10 min titrate in a clear-glass vessel with 0.01 mol/l sodium thiosulfate until colourless.

Then acidify with 10 ml phosphoric acid, and titrate the iodine liberated with 0.01 mol/l sodium thiosulfate. The amount of chlorine corresponding to the titration after the acidification (in the absence of other iodine-liberating substances) is designated organically bound chlorine.

Calculation

Chlorine consumption = difference of mg/l Cl_2 added (calculated from the number of ml corresponding to the chlorine demand + 3 ml chlorine water (0.1%) − mg/l Cl_2 (calculated from the number of ml 0.01 mol/l sodium thiosulfate consumed before the acidification). Organically bound chlorine (as amines): mg/l Cl_2, calculated from the number of ml 0.01 mol/l sodium thiosulfate consumed after the acidification.

1 ml 0.01 mol/l sodium thiosulfate solution $\triangleq$ 0.355 mg Cl_2.

Reporting of results

The values are rounded off to 0.1 mg/l Cl_2.

Reagent preparations

See the reagent solutions under Chlorine demand, and:
Phosphoric acid (25%): Dilute 170 ml ortho-Phosphoric acid min. 85% (about 1.71) GR with deionised water to make 1000 ml.

Reagents

See the reagents under Chlorine demand, and:

Cat. No.		Packages
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l

Chromium

Qualitative analysis

When in a solution of sulfuric acid with diphenylcarbazide, chromium(VI) ions produce a reddish-violet colour.

Rapid determination possible with Merckoquant® Test Strips and Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative analysis

Chromium compounds can be present in water in the trivalent form as chromium(III) ions and in the hexavalent form as chromate or dichromate ions. With the following methods it is possible to determine the content of total chromium and of chromate or dichromate ions. The content of chromium(III) ions is given by the difference between total chromium and chromate or dichromate ions.

1. Photometric determination of the total chromium with diphenylcarbazide

Suitable for the determination of total chromium content in concentrations between 1 and 20 mg/l Cr.

Interferences and pre-treatment

Organic substances, dyes and heavy metal ions interfere.

To eliminate organic substances, treat 100 ml of the water sample with 10 ml sodium hydroxide solution (pH of the solution about 11), and then with potassium permanganate solution until the red colour persists. Then boil for 10 min, and reduce the excess potassium permanganate with a few drops of methanol. After cooling, add sufficient hydrochloric acid to bring the precipitated metallic hydroxides into solution again and give the solution an acid reaction. Add 10 ml di-sodium hydrogen phosphate solution (or more, if necessary) and 10 ml sodium hydroxide solution to precipitate interfering heavy metal ions. Make up the sample to 200 ml with deionised water (in the case of more than 10 mg/l total chromium, to 500 ml).

Procedure

After the precipitate in the pre-treated sample has settled, pipette sufficient of the supernatant liquid to contain between 10 and 150 μg chromium into a 100-ml volumetric flask. Add 2 ml phosphoric acid and 2 ml diphenylcarbazide solution, make up to 100 ml with deionised water, and after 5 to 30 min (when the colour intensity has become constant) measure at 550 nm against a blank of deionised water treated in the same manner.

The reference curve is prepared from standard solutions of potassium chromate or dilution solutions of Chromium standard solution Titrisol treated in the same manner as the water sample.

Calculation

$$\text{mg/l Cr (total chromium)} = \frac{\text{mg Cr} \times b \times 1000}{a \times c}$$

mg Cr = value read from the reference curve for the absolute content of chromium

a = ml of test water used

b = volume, in ml, to which the sample was made up after the pre-treatment

c = volume, in ml, of the supernatant clear liquid removed with pipette

1 mmol chromium(III/VI) ions ≙ 51.996 mg

1 meq chromium(III) ions ≙ 17.332 mg Cr^{3+}

1 meq chromium(VI) ions ≙ 8.666 mg Cr^{6+}

1 mg Cr ≙ 2.23 mg CrO_4^{2-}

1 mg CrO_4^{2-} ≙ 0.45 mg Cr

Reporting of results

The values are rounded off to 0.1 mg/l for less than 10 mg/l, and to 1 mg/l for 10 mg/l or higher.

Reagent preparations

Chromium standard solution: Dissolve 3.740 g Potassium chromate GR in deionised water and make up to 1000 ml.
1 ml ≙ 1 mg Cr.

Chromium standard solution: Dilute the contents of one ampoule of Chromium standard solution Titrisol with deionised water to make 1000 ml.
1 ml ≙ 1 mg Cr.

The dilutions of the chromium standard solution required for plotting of the reference curve should be freshly prepared.

Diphenylcarbazide solution: Dissolve 1 g 1,5-Diphenylcarbazide GR and redox indicator in 100 ml Acetone GR, and add 1 drop glacial acetic acid. Store the solution in a brown bottle.

Potassium permanganate solution: Dissolve 40 g Potassium permanganate GR in 1000 ml deionised water.

di-Sodium hydrogen phosphate solution: Dissolve 100 g di-Sodium hydrogen phosphate 12-hydrate GR in 900 ml deionised water.

Sodium hydroxide solution 2 mol/l: Make the contents of one ampoule of 1 mol/l Sodium hydroxide solution Titrisol concentrated solution for preparation of 1 litre of 1 N solution up to 500 ml with deionised water.

Phosphoric acid: Mix 700 ml ortho-Phosphoric acid min. 85% (about 1.71) GR with 300 ml deionised water.

Hydrochloric acid 2 mol/l: Make the contents of one ampoule of 1 mol/l Hydrochloric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution up to 500 ml with deionised water.

Reagents

Cat. No.		Packages
14	Acetone GR	1 l, 2½ l
9531	Acilit® indicator strips pH 0–6.0 non-bleeding graduated in 0.5 pH units	1 pack
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack

9948	Chromium standard solution Titrisol® 1.000 g ± 0.002 g Cr ($CrCl_3$ in dil. HCl)	1 amp.
3091	1,5-Diphenylcarbazide GR and redox indicator	25 g, 100 g
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
4952	Potassium chromate GR	250 g, 1 kg
5082	Potassium permanganate GR	250 g, 1 kg, 5 kg
6009	Methanol GR	1 l, 2½ l
6579	di-Sodium hydrogen phosphate 12-hydrate GR	500 g, 1 kg, 5 kg
9956	Sodium hydroxide solution 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9136	Sodium hydroxide solution 2 mol/l	1 l
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
9970	Hydrochloric acid 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.

2. Photometric determination of the total chromium with diphenylcarbazide after prior oxidative fusion

Suitable for determination of the total chromium content in concentrations greater than 1 mg Cr/l and in the presence of larger amounts of accompanying substances difficult to oxidise.

Interferences and pre-treatment

Larger amounts of manganese can mask the pure yellow colour of chromates by the green colour of manganates.

Acidify 100 ml of the sample with 1–2 drops of phosphoric acid, and concentrate in a glass beaker. Transfer the concentrate quantitatively to an Alsint crucible and evaporate to dryness. Add 3 spatula-tips of oxidation mixture, and heat until the melt is clear. Boil the cooled crucible in 100 ml deionised water until the melt is completely dissolved. If it is coloured green as a result of larger amounts of manganese, boil until the colour has disappeared with formation of manganese dioxide. Filter the solution quantitatively into a 200-ml volumetric flask, or in the case of more than 10 mg/l total chromium, into a 500-ml flask, and make up to the mark with deionised water.

Procedure

Pipette sufficient of the pre-treated solution to contain between 10 and 150 µg chromium into a 100-ml volumetric flask. Neutralise the sample with phosphoric acid, treat with a further 2 ml of phosphoric acid and 2 ml diphenylcarbazide solution, and make up to 100 ml with deionised water. After 5 to 30 min reaction time (when the intensity of colour has become constant), measure the absorbance at 550 nm against a blank of deionised water treated in the same manner.

The reference curve is prepared from standard solutions of potassium chromate or dilution solutions of Chromium standard solution Titrisol treated in the same manner as the water sample.

Calculation

$$\text{mg/l Cr (total chromium)} = \frac{\text{mg Cr} \times \text{b} \times 1000}{\text{a} \times \text{c}}$$

mg Cr = value read from the reference curve for the absolute content of chromium
a = ml of test water used
b = volume, in ml, of the flask into which the solution of the oxidative melt was filtered
c = volume, in ml, of filtrate pipetted into the 100-ml-flask

Reporting of results

As under 1.

Reagent preparations

Chromium standard solution: As under 1.
Diphenylcarbazide solution: As under 1.
Oxidation mixture: Throughly mix 2 parts by weight of Potassium carbonate/sodium carbonate GR and 1 part by weight Potassium chlorate GR.
Phosphoric acid: As under 1.

Reagents

Cat. No.		Packages
14	Acetone GR	1 l, 2½ l
9948	Chromium standard solution Titrisol® 1.000 g ± 0.002 g Cr ($CrCl_3$ in dil. HCl)	1 amp.

Cat. No.		
3091	1,5-Diphenylcarbazide GR and redox indicator	25 g, 100 g
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
6683	Potassium carbonate/sodium carbonate GR	500 g, 2½ kg
4944	Potassium chlorate GR	500 g
4952	Potassium chromate GR	250 g, 1 kg
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l

3. Photometric determination of the chromate ions with diphenylcarbazide

Suitable for determination of the chromate ions in concentrations of about 1 to 20 mg/l Cr.

Interferences and pre-treatment

Larger amounts of organic substances, dyestuffs and heavy metal ions, particularly iron(III) ions, interfere; also oxidising and reducing substances such as, for example, free chlorine or sulfite ions.

In order to exclude oxidising substances, add 25 ml di-sodium hydrogen phosphate solution and sodium hydroxide pellets to 250 ml of test water until the sample gives an alkaline reaction. Then add 10 ml methanol, and make up to 500 ml with deionised water. Carry out the determination on the following day.

In order to exclude the influence of reducing substances, carry out a preliminary test by adding 3 ml sulfuric acid and 5 drops of methyl orange solution to 100 ml of the water, and titrating dropwise with sodium hypochlorite solution until the red colour disappears.

To the 100 ml test water intended for determination add 10 ml di-sodium hydrogen phosphate solution, about 5 sodium hydroxide pellets and 1 ml sodium hypochlorite solution more than in the preliminary test, in the order given. Mix well, add 5 ml methanol, and make up to 200 ml with deionised water. Carry out the determination on the following day.

Procedure

Pipette sufficient of the pre-treated sample to contain between 10 and 150 μg chromium into a 100-ml volumetric flask. Add 2 ml phosphoric acid and 2 ml diphenylcarbazide solution, make up to 100 ml with deionised water, and after

5 to 30 min (when the intensity of colour has become constant) measure at 550 nm against a blank of deionised water treated in the same manner.

The reference curve is prepared from standard solutions of potassium chromate or dilution solutions of Chromium standard solution Titrisol treated in the same manner as the test water.

Calculation

$$\text{mg/l Cr (chromate)} = \frac{\text{mg Cr} \times 2 \times 1000}{a}$$

mg Cr = value read from the calibration curve for the absolute content of chromium
2 = factor to take into account the dilution of the water sample during the pretreatment
a = volume, in ml, of the pre-treated sample pipetted into the 100-ml flask

Reporting of results

As under 1.

Reagent preparations

Chromium standard solution: As under 1.
Diphenylcarbazide solution: As under 1.
di-Sodium hydrogen phosphate solution: As under 1.
Phosphoric acid: As under 1.
Sulfuric acid: Add 100 ml Sulfuric acid 95–97% (about 1.84) GR carefully to 300 ml deionised water.

Reagents

Cat. No.		Packages
14	Acetone GR	1 l, 2½ l
9948	Chromium standard solution Titrisol® 1.000 g ± 0.002 g Cr ($CrCl_3$ in dil. HCl)	1 amp.
3091	1,5-Diphenylcarbazide GR and redox indicator	25 g, 100 g
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
4952	Potassium chromate GR	250 g, 1 kg
6009	Methanol GR	1 l, 2½ l

Cat. No.		
1323	Methyl orange solution 0.1% indicator	250 ml, 1 l
6579	di-Sodium hydrogen phosphate 12-hydrate GR	500 g, 1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
5614	Sodium hypochlorite solution techn. (about 13% active chlorine)	55 kg
573	ortho-Phosphoric acid min. 85% (about 1.71)	1 l, 2½ l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

Rapid photometric analysis possible with Spectroquant® Chromium
see Appendix

Copper

Qualitative analysis

1. For detection of low concentrations of copper treat 1–5 ml of the neutral or weakly acid water sample with 1–2 ml sodium acetate solution and a spatula-tip (about 20–30 mg) of ascorbic acid, and shake. Then add 1–2 drops of bathocuproinedisulfonic acid disodium salt solution. A yellow to reddish-orange colour is produced, depending on the copper ion content.

2. For detection of higher concentrations add 1 ml sulfuric acid and 1 g potassium peroxodisulfate to 100 ml of the water sample, and evaporate. Add a large excess of ammonia solution, and – where necessary – filter. A blue colour indicates the presence of copper(II) ions.

Lower limit of detection: 0.5 mg/l Cu^{2+} in a 20-cm layer.

Reagent preparations

Bathocuproinedisulfonic acid disodium salt solution: Dissolve 0.1 g Bathocuproinedisulfonic acid disodium salt GR in 2 ml acetic acid, and add 25 ml deionised water.

Sodium acetate solution, saturated: Dissolve 52.6 g Sodium acetate cryst. GR indifferent to potassium permanganate in sufficient deionised water to make 100 ml.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
127	L(+)Ascorbic acid GR	100 g, 250 g, 1 kg
24518	Bathocuproinedisulfonic acid disodium salt (2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid disodium salt) GR	100 mg, 1 g, 5 g

Cat. No.		Packages
62	Acetic acid glacial 96% (about 1.06) GR	1 l
5091	Potassium peroxodisulfate GR	250 g, 1 kg
6267	Sodium acetate cryst. GR indifferent to potassium permanganate	500 g, 1 kg, 5 kg
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

Rapid determination possible with Merckoquant® Test Strips and Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative analysis

1. Gravimetrically with quinaldic acid as copper quinaldate

Suitable for determination of copper ions in concentrations greater than 2 mg/l Cu^{2+}.

Interferences and pre-treatment

Water containing cyanide complexes and larger amounts of organic substances is evaporated, and fumed to dryness with concentrated sulfuric acid and nitric acid. The residue is taken up in 150 ml deionised water.

Smaller amounts of iron ions are converted to the trivalent form with Perhydrol, and kept in solution with tartaric acid.

Larger amounts of iron ions are precipitated with an excess of ammonia solution under addition of Perhydrol, thus separating them from the copper. The filtrate is evaporated and neutralised where necessary.

Procedure

Heat 150 ml of the neutral and – where necessary – pre-treated water sample, which should contain at least 1 mg copper ions, to boiling with 5 ml 1 mol/l sulfuric acid, and precipitate the copper ions by stirring vigorously with quinaldic acid solution. The resulting green precipitate settles rapidly. Check with a few drops of quinaldic acid solution that precipitation is complete, and allow to stand for 30 min. Then filter the precipitate through a glass filter-crucible (G 3), wash with hot deionised water, and dry to constant weight at 125° C (about 3 hours).

Calculation

1 mg copper quinaldate $\triangleq$ 0.150 mg Cu^{2+}

$$\text{mg/l } Cu^{2+} = \frac{150 \times a}{b}$$

a = mg copper quinaldate
b = ml of test water used
1 mmol copper(II) ions $\hat{=}$ 63.546 mg Cu^{2+}
1 meq copper(II) ions $\hat{=}$ 31.77 mg Cu^{2+}

Reporting of results

The values are rounded off to 0.5 mg/l.

Reagent preparations

Quinaldic acid solution: Dissolve 3 g Quinaldic acid GR in 100 ml deionised water.

Sulfuric acid 1 mol/l: Dilute the contents of one ampoule 0.5 mol/l Sulfuric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution to 500 ml with deionised water.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
216	Quinaldic acid GR (reagent for cadmium, iron, copper, uranium and zinc)	5 g
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
454	Nitric acid min. 65% (about 1.40) GR	1 l, 2½ l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
9981	Sulfuric acid 0.5 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
804	L(+) Tartaric acid GR	250 g, 1 kg, 5 kg

2. Photometrically with zinc N,N-dibenzyldithiocarbamate

Suitable for determination of copper(II) ions in concentrations between 0.001 and about 0.3 mg/l (particularly in power-station waters). At higher concentrations the test water should be diluted with copper-free deionised water.

Interferences and pre-treatment

If in addition to copper(II) ions copper(I) ions and copper oxide particles are also present in the water sample the latter can be partially co-determined under certain circumstances.

Too high a result for copper(II) ions is also found if the test water contains a multiple of molybdenum(VI) ions or tin(II) ions in comparison with copper(II) ions.

The presence of hydrazine or morpholine in combination with higher concentrations of copper(II) ions can likewise yield results which are too high.

All the glass apparatus used in the determination should be rinsed out with dilute nitric acid before use.

Procedure

Introduce 3 ml nitric acid into a 250-ml volumetric flask, and make up to the mark with the test water. Then transfer completely to a 500-ml separating funnel, and treat with 5 ml hydrochloric acid. Add 15 ml zinc N,N-dibenzyldithiocarbamate solution, shake vigorously for 1 min, and after separation of the phases filter into a quartz cell. Cover the latter immediately. Measure at 436 nm against carbon tetrachloride. If quartz cells are not available, carry out each measurement twice, exchanging the sample cell and the comparison cell with one another. Use the mean value of the two measurements in reading off the reference curve.

The reference curve is prepared from standard solutions of metallic copper or dilution solutions of Copper standard solution Titrisol treated in the same manner as the test water.

The blank value due to the reagents added is determined from two samples of copper-free deionised water. The amounts of reagents specified above are added to the first sample, and double the amounts to the second. The blank value is given by the difference in the values measured for the two solutions.

Calculation

mg/l Cu^{2+} = A − B
A = mg/l Cu^{2+}/l (disregarding the blank value)
B = blank value determined in mg/l Cu^{2+}
1 mmol copper(II) ions = 63.546 mg Cu^{2+}
1 meq copper(II) ions ≙ 31.77 mg Cu^{2+}

Reporting of results

The values are rounded off to 0.001 mg/l for a copper(II) ion content from 0.001 to 0.1 mg/l, and to 0.01 mg/l from 0.1 to 10.0 mg/l.

Reagent preparations

Copper standard solution: Prepare the solution and its dilutions with freshly boiled and cooled deionised water.

Dissolve 1.000 g Copper powder GR in 3 ml Nitric acid min. 65% (about 1.40) GR and 3 ml deionised water. Add 1 ml Sulfuric acid 95–97% (about 1.84) GR, and evaporate the solution almost to dryness. Take the residue up with deionised water, and make up to 1000 ml. 1 ml ≙ 1 mg Cu^{2+}.

Copper standard solution: Dilute the contents of one ampoule of Copper standard solution Titrisol to 1000 ml with deionised water. 1 ml ≙ 1 mg Cu^{2+}.

The dilutions required for plotting of the reference curve should be freshly prepared from the standard solution.

Zinc N,N-dibenzyldithiocarbamate solution: Dissolve 0.5 g N,N-dibenzyldithiocarbamic acid zinc salt GR in 500 ml Carbon tetrachloride GR. The solution is stable for about 4 weeks when stored in a brown glass-stoppered bottle.

Nitric acid, dilute: Mix 100 ml Nitric acid min. 65% (about 1.40) GR with 300 ml deionised water.

Reagents

Cat. No.		Packages
3460	N,N-Dibenzyldithiocarbamic acid zinc salt GR	25 g
2703	Copper fine powder GR	250 g, 1 kg
9987	Copper standard solution Titrisol® 1.000 g ± 0.002 g Cu ($CuCl_2$ in water)	1 amp.
456	Nitric acid min. 65% (about 1.40) tested by the dithizone method GR	1 l, 2½ l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
2208	Carbon tetrachloride GR (for determinations with dithizone)	1 l, 2½ l

3. Photometrically by means of sodium diethyldithiocarbamate

Suitable for determination of copper(II) ions in concentrations between 0.01 and about 2 mg/l.

Interferences and pre-treatment

Copper cyanide compounds are decomposed by fuming with sulfuric acid (about 1.84) and hydrogen peroxide solution. The solution is evaporated to dryness, and the residue taken up with copper-free deionised water.

The interfering influence of small amounts of iron ions is eliminated by addition of citric acid solution (see Procedure).

Zinc and lead ions in larger amounts cause a white turbidity.

Chromium in concentrations above about 10 mg/l yields low values.

In the presence of nickel the copper concentration determined is corrected: 10 μg Ni is equivalent to 1 μg Cu.

Discoloured water samples are extracted with chloroform to remove the dyestuffs. All the glass apparatus used for the determination should be rinsed out before use with dilute nitric acid.

Procedure

Introduce 100 ml of the water sample, or depending on the copper concentration a smaller volume made up to 100 ml with deionised water, into a separating funnel, add 1 ml citric acid solution, 0.5 ml sulfuric acid, 0.5 ml ammonium chloride solution and 10 ml chloroform in that order, and shake evenly for 5 min. Drain off the chloroform extract, and discard. Treat the aqueous phase with 2 ml sodium diethyldithiocarbamate solution and 25 ml chloroform, and shake for 10 min. Filter the organic phase through a small, dry filter paper directly into the cell or into a glass-stoppered, well-closable vessel, and measure at 440 nm against a blank of 100 ml copper-free deionised water treated in the same manner.

The reference curve is prepared from standard solutions of metallic copper or dilution solutions of Copper standard solution Titrisol treated in the same manner as the water sample.

Calculation

A possible dilution of the water sample to a starting volume of 100 ml is to be taken into account in the calculation.

1 mmol copper(II) ions ≙ 63.546 mg Cu^{2+}.

1 meq copper(II) ions ≙ 31.77 mg Cu^{2+}.

Reporting of results

The values are rounded off to 0.01 mg/l.

Reagent preparations

All the solutions are prepared with copper-free deionised water.

Ammonium chloride solution: Dissolve 20 g Ammonium chloride GR in 80 ml deionised water.

Citric acid solution: Dissolve 20 g Citric acid GR in 80 ml deionised water.

Copper standard solution: Dissolve 1.000 g Copper powder GR in 3 ml Nitric acid min. 65% (about 1.40) GR and 3 ml deionised water. Add 1 ml Sulfuric acid 95–97% (about 1.84) GR, and fume the solution almost to dryness. Take the residue up with deionised water, and make up to 1000 ml. 1 ml $\triangleq$ 1 mg Cu^{2+}.

The dilutions required for plotting of the reference curve should be freshly prepared from the standard solution.

Sodium diethyldithiocarbamate solution: Dissolve 1 g Sodium diethyldithiocarbamate GR in 100 ml deionised water. The solution is stable for about 1 month.

Nitric acid, dilute: Mix 100 ml Nitric acid min. 65% (about 1.40) GR with 300 ml deionised water.

Sulfuric acid (about 1.27): Carefully pour 100 ml Sulfuric acid 95–97% (about 1.84) GR into 300 ml deionised water.

Hydrogen peroxide solution: Dilute 10 ml Perhydrol 30% H_2O_2 with deionised water to make 100 ml.

Reagents

Cat. No.		Packages
1145	Ammonium chloride GR	500 g, 1 kg, 5 kg
2442	Chloroform GR (for determinations with dithizone)	1 l, 2½ l
244	Citric acid 1-hydrate GR	500 g, 1 kg, 5 kg
2703	Copper fine powder GR	250 g, 1 kg
9987	Copper standard solution Titrisol® 1.000 g ± 0.002 g Cu ($CuCl_2$ in water)	1 amp.
6689	Sodium diethyldithiocarbamate (trihydrate) GR (reagent for copper)	25 g, 100 g
7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
454	Nitric acid min. 65% (about 1.40) GR	1 l, 2½ l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

Rapid photometric analysis possible with Spectroquant® Copper
see Appendix

Cyanide

1.1. Qualitative analysis with chloramine T/barbituric acid

Treat 100 ml of ice-cooled test water in a separating funnel with 1 ml iron(III) chloride solution, 50 ml ice-cooled hydrochloric acid and 15 ml iso-butyl methyl ketone in that order, and shake for 1 min. After the phases have separated, use the aqueous layer for detection of cyanide ions, and the ketone layer for detection of thiocyanate ions.

1. Detection of cyanides

Add 5 ml sodium hydroxide solution to 5 ml of the aqueous phase slowly and with shaking. Treat the solution with 1 drop of phenolphthalein solution, and subsequently with 1 mol/l hydrochloric acid until the colour changes. Then add 20 ml buffer solution, 1 ml chloramine T solution and 3 ml reagent solution. A red colour is produced in the presence of cyanide ions.

Lower limit of detection: about 0.05 mg/l CN^-.

2. Detection of thiocyanates

Shake the ketone phase with 10 ml 0.1 mol/l hydrochloric acid for 1 min. After separation of the phases, discard the ketone layer. A red colour is produced in the hydrochloric acid phase when thiocyanate ions are present.

Lower limit of detection: about 0.1 mg/l SCN^-.

Reagent preparations

Chloramine T solution: Dissolve 1 g Chloramine T GR in deionised water and make up to 100 ml.

Iron(III) chloride solution: Dissolve 1 g Iron(III) chloride GR in deionised water and make up to 100 ml.

Sodium hydroxide solution: Dissolve 15 g Sodium hydroxide pellets GR in deionised water and make up to 100 ml.

Buffer solution: either from Buffer Titrisol for preparation of 500 ml of buffer solution pH 7.00 or Buffer solution ready for use pH 7.00.

Reagent solution: Slurry 6 g Barbituric acid GR with a little deionised water, and add 30 ml Pyridine GR and 60 ml deionised water to dissolve. Then add 6 ml Hydrochloric acid min. 32% (about 1.16) GR. The pyridine should be practically colourless, otherwise it should be freshly distilled (B.pt. 115–118° C).

Reagents

Cat. No.		Packages
132	Barbituric acid GR	25 g, 100 g
6146	iso-Butyl methyl ketone for extraction analysis	1 l, 2½ l
2426	Chloramine T (trihydrate) GR	250 g, 1 kg
3943	Iron(III) chloride GR	250 g, 1 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
7227	Phenolphthalein solution 1% in ethanol indicator	250 ml, 1 l
9439	Buffer solution ready for use pH 7.00 (phosphate)	1 l
9887	Buffer-Titrisol® concentrated solution for preparation of 500 ml of buffer solution pH 7.00 (phosphate)	1 amp.
9728	Pyridine GR	500 ml, 1 l, 2½ l
319	Hydrochloric acid min. 32% (about 1.16) GR	1 l, 2½ l
9973	Hydrochloric acid 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9060	Hydrochloric acid 0.1 mol/l	1 l, 5 l
9970	Hydrochloric acid 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9057	Hydrochloric acid 1 mol/l	1 l, 5 l

1.2. Qualitative analysis by the Prussian blue reaction

Mix about 10 ml test water with 1 ml iron(II) sulfate solution and 1 ml potassium carbonate solution, and then acidify with sulfuric acid. In the presence of cyanide ions a blue colour to blue precipitate of the dyestuff is produced depending on the concentration. At concentrations of less than 5 mg/l CN^- and in the presence of some heavy metal cyanide complexes, this method of detection fails. In the case of waters with reducing constituents the development of the blue colour can be accelerated by addition of a few drops of iron(III) chloride solution.

Reagent preparations

Iron(III) chloride solution: Dissolve 10 g Iron(III) chloride GR in 90 ml deionised water.

Iron(II) sulfate solution: Dissolve 10 g Iron(II) sulfate GR in 90 ml deionised water.

Potassium carbonate solution: Dissolve 5 g Potassium carbonate GR in 95 ml deionised water.

Sulfuric acid: Carefully pour 1 part by volume Sulfuric acid 95–97% (about 1.84) GR into 19 parts deionised water.

Reagents

Cat. No.		Packages
3943	Iron(III) chloride GR	250 g, 1 kg
3965	Iron(II) sulfate GR	500 g, 1 kg, 5 kg
4928	Potassium carbonate GR	500 g, 1 kg, 5 kg
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

Rapid determination possible with Merckoquant® Test Strips and with Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative determination

1. Distillation for determination of the total cyanides

Suitable for determination of the total cyanides in concentrations of 0.2 to 1000 mg/l CN^-.

All complex cyanide compounds including those of di- and trivalent iron are decomposed quantitatively to hydrogen cyanide with the exception of the hexacyanocobaltate(III) ion, which is only about 20% decomposed.

Stabilisation of the cyanide concentration after sampling

Introduce 500 ml of the test water into a 500-ml flask, and add a few drops of phenolphthalein solution. If the water is colourless or only a faint pink colour, add 5 ml 1 mol/l sodium hydroxide. Then add a few drops of redox indicator solution, and pipette in ascorbic acid solution with swirling until the blue colour has disappeared. If the solution is then a red colour, an adequate excess of alkali was present. If on the other hand the solution becomes colourless, the pre-treatment must be repeated with addition of a larger amount of 1 mol/l sodium hydroxide. Then add 2 ml ascorbic acid solution in excess.

If the water is strongly coloured or has a very high content of heavy metal ions, the change in the redox indicator is not detectable. In such cases, adjust the pH value of the water to about 11 with 1 mol/l sodium hydroxide. Then add an excess of ascorbic acid solution in 2-ml portions by testing with potassium iodide-starch paper and pipetting in an additional 2 ml ascorbic acid solution.

Interferences and pre-treatment

Cyanate and thiocyanate ions do not affect the determination.

Sulfides, which would evolve hydrogen sulfide during the distillation, are precipitated with cadmium nitrate solution and the precipitate filtered off.

Sulfite ions in concentrations up to 500 mg/l SO_3^{2-} and carbonate and hydrogen carbonate ions, which are decomposed to carbon dioxide by the acid action and absorbed in the washer, do not interfere as long as the contents of the receiver for the absorption of hydrogen cyanide are sufficiently alkaline.

Nitrite ions in concentrations greater than 500 mg/l NO_2^- yield low values from the distillation. In this case the test water must be diluted below such concentration.

The presence of chlorine or active compounds of chloride leads to low values. Up to 400 mg/l active chlorine can be excluded by addition of 25 ml ascorbic acid solution per 500 ml water.

Cyanogen chloride does not interfere in the determination after the preparation by distillation.

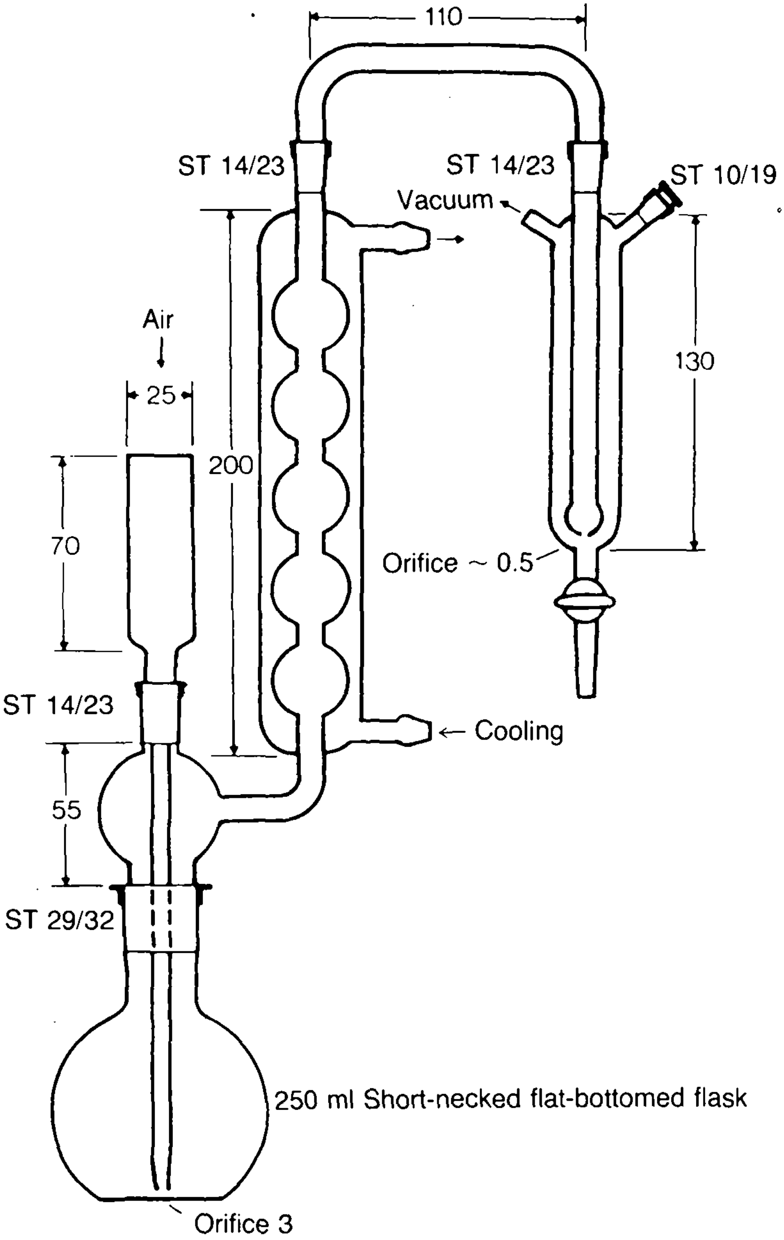
Distillation

The distillation is carried out in the apparatus illustrated on page 74.

Charge the washer with 20 ml 1 mol/l sodium hydroxide. Assemble the apparatus, and suction a current of air through at the rate of 5–10 bubbles per second (monitored at the washer). Add 10 ml Titriplex III solution and 100 ml pre-treated water through the filling and aerating tube. (The amounts of reagent solutions added during the pre-treatment are to be taken into account in the test water volume.) Add 5 drops of methyl orange solution, 2 mol/l hydrochloric acid until the colour changes, and 10 ml of the acid in excess.

Heat up the distillation flask for 5–10 min, then boil for 30 min under reflux and passing through of air at 5–10 bubbles per second.

Without interrupting the distillation, add 10 ml magnesium chloride solution and 15 ml 4 mol/l sodium hydroxide through the filling tube, and boil for a further 20 min.


110
ST 14/23
ST 14/23
ST 10/19
Vacuum
Air
25
200
130
70
Orifice ~ 0.5
ST 14/23
Cooling
55
ST 29/32
250 ml Short-necked flat-bottomed flask
Orifice 3

Then very carefully add 30 ml sulfuric acid, and distill for 90 min. Drain the alkaline distillate into a 100-ml volumetric flask, rinse the washer out with deionised water, and make the flask up to the mark. This solution serves for photometric or titrimetric determination of the total cyanide ions depending on their concentration (see under 3. and 4.).

Reagent preparations

Ascorbic acid solution: Dissolve 2 g L(+)Ascorbic acid GR in 100 ml deionised water.

Cadmium nitrate solution: Dissolve 10 g Cadmium nitrate 4-hydrate GR in 90 ml deionised water.

Magnesium chloride solution: Dissolve 510 g Magnesium chloride GR in 1000 ml deionised water.

Sodium hydroxide 4 mol/l: Make the contents of one ampoule of 1 N Sodium hydroxide solution Titrisol concentrated solution for preparation of 1 litre of 1 N solution up to 250 ml with deionised water or dissolve 160 g Sodium hydroxide pellets GR in deionised water, and make up to 1000 ml.

Redox indicator solution: Dissolve 0.1 g 2,6-Dichlorophenolindophenol sodium salt (dihydrate) GR (for determination of ascorbic acid) in 100 ml deionised water. Stored in a dark bottle the solution is stable for about 1 week.

Hydrochloric acid 2 mol/l: Make the contents of one ampoule of 1 mol/l Hydrochloric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution up to 500 ml with deionised water.

Sulfuric acid: Carefully pour 500 ml Sulfuric acid 95–97% (about 1.84) GR into 500 ml deionised water.

Titriplex III solution: Dissolve 10 g Titriplex III in 90 deionised water.

Reagents

Cat. No.		Packages
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
127	L(+)Ascorbic acid GR	100 g, 250 g, 1 kg
2019	Cadmium nitrate 4-hydrate GR	250 g
3028	2,6-Dichlorophenolindophenol sodium salt (dihydrate) GR (for determination of ascorbic acid)	5 g, 25 g
9512	Potassium iodide-starch paper (for detection of ozone)	1 pack

5833	Magnesium chloride GR	250 g, 1 kg, 5 kg
1323	Methyl orange solution 0.1% indicator	250 ml, 1 l
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
9956	Sodium hydroxide solution 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9137	Sodium hydroxide solution 1 mol/l	1 l, 50 l
7227	Phenolphthalein solution 1% in ethanol indicator	250 ml, 1 l
9970	Hydrochloric acid 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
8418	Titriplex® III [(ethylenedinitrilo)tetraacetic acid disodium salt] (dihydrate) GR	100 g, 250 g, 1 kg, 5 kg

2. Distillation for determination of the decomposable cyanide

Suitable for determination of the decomposable cyanide in concentrations up to 1000 mg/l CN^-.

The cyanides decomposable by chlorine or catalytic action (alkali cyanides, cyanide complexes of zinc, cadmium, copper, silver and nickel) are decomposed and separated from the practically non-decomposable cyanides of di- and trivalent iron. The proportion of the iron cyanide complexes decomposed depends on the concentration of the latter.

Stabilisation of the cyanide concentration after sampling

As described under 1.

Interferences and pre-treatment

The interfering factors are excluded as described under 1. Interference from sulfide ions is eliminated by addition of lead acetate solution to the distillation flask.

Distillation

The distillation is carried out in the apparatus described under 1.

Add a few drops of methyl orange solution to 100 ml of the pre-treated test water, titrate with 1 mol/l hydrochloric acid until the colour changes, and note the consumption.

Charge the washer with 20 ml 1 mol/l sodium hydroxide, assemble the apparatus, and suction through a current of air at the rate of 5–10 bubbles per second (monitored at the washer). Introduce 10 ml zinc acetate solution, 10 ml lead acetate solution, 25 ml buffer solution and 100 ml of the pre-treated water into the distillation flask through the filling and aerating tube, and likewise the recorded consumption of 1 mol/l hydrochloric acid. Heat the contents of the flask to boiling and distill for 45 min under reflux. Without interrupting the distillation, wash 0.2 g zinc dust (preferably with a dosing spoon) through the filling tube with a little deionised water. Distill for a further 45 min, drain the alkaline wash solution into a 100-ml volumetric flask, rinse the washer with deionised water and make the flask up to the mark. The cyanide ions decomposable by chlorine or catalytic action are determined photometrically or titrimetrically depending on the concentration (see under 3. and 4.).

Evaluation of the calculations under 3. and 4.

At a higher concentration of iron cyanide complexes in the sample a correction must be made to the value for the cyanide decomposable by chlorine: The difference between the concentration of total cyanide and of the cyanide decomposable by chlorine gives the concentration of cyanide not decomposable by chlorine. The correction for the decomposable proportion corresponding to the concentration of the cyanide not decomposable by chlorine is read from the correction curve illustrated, and subtracted from the concentration of the cyanide decomposable by chlorine.

Reagent preparations

Ascorbic acid solution: Dissolve 2 g L(+)Ascorbic acid GR in 100 ml deionised water.

Buffer solution: Dissolve 200 g Sodium hydroxide pellets GR and 240 g Citric acid GR in 400 ml deionised water in each case. Combine the two solutions carefully with cooling, and add 170 ml glacial acetic acid.

Redox indicator solution: Dissolve 0.1 g 2,6-Dichlorophenolindophenol sodium salt GR (for determination of ascorbic acid) in 100 ml deionised water. Stored in a dark bottle the solution is stable for about 1 week.

Zinc acetate solution: Dissolve 100 g Zinc acetate GR in 200 ml deionised water.

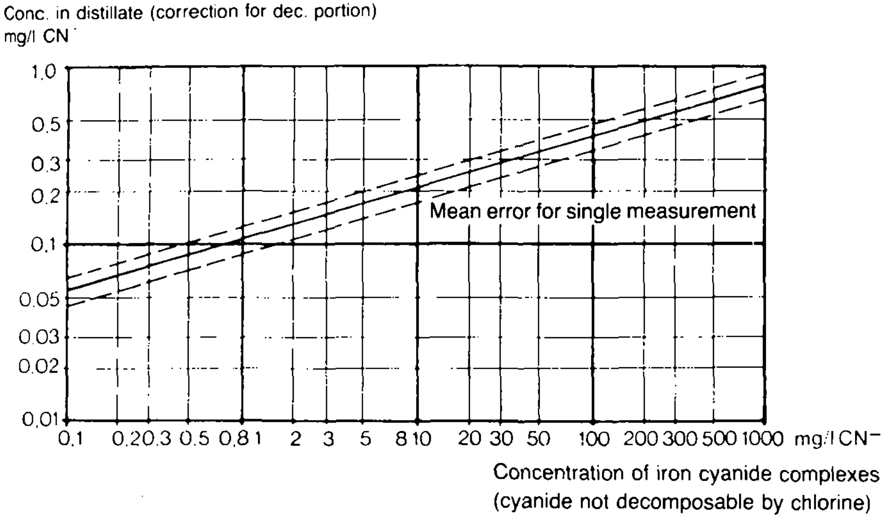


Fig.: Correction curve for taking into account the content of iron cyanide complexes in determination of the decomposable cyanide.

Reagents

Cat. No.		Packages
9532	Alkalit® Indicator strips pH 7.5–14 non-bleeding graduated in 0.5 units	1 pack
127	L(+)Ascorbic acid GR	100 g, 250 g, 1 kg
7375	Lead(II) acetate 3-hydrate GR	250 g, 1 kg
244	Citric acid 1-hydrate GR	500 g, 1 kg, 5 kg
3028	2,6-Dichlorophenolindophenol sodium salt (dihydrate) GR (for determination of ascorbic acid)	5 g, 25 g
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
9512	Potassium iodide-starch paper (for detection of ozone)	1 pack
1323	Methyl orange solution 1% indicator	250 ml, 1 l
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
9956	Sodium hydroxide solution 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9137	Sodium hydroxide solution 1 mol/l	1 l, 50 l
7227	Phenolphthalein solution 1% in ethanol indicator	250 ml, 1 l
9970	Hydrochloric acid 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9057	Hydrochloric acid 1 mol/l	1 l, 5 l, 50 l
8789	Zinc powder GR	500 g, 1 kg
8802	Zinc acetate GR	250 g, 1 kg

3. Photometric determination by means of barbituric acid / pyridine

Suitable for determination of cyanide ions in concentrations from 0.02 to 2 mg/l CN^-. Higher concentrations require a dilution of the distillate.

Interferences and pre-treatment

The interference of higher concentrations of sulfides is excluded during the distillations under 1. and 2.

Procedure

Pipette 10–25 ml of the made-up distillate according to cyanide ion content into a 100-ml volumetric flask. In the case of cyanide concentrations greater than 2 mg/l CN^-, dilute an aliquot portion of the distillate 1 : 10 with 0.2 mol/l sodium hydroxide, and pipette 10–25 ml of this dilution into a 100-ml volumetric flask. Where necessary, make up the volume to 25 ml with 0.2 mol/l sodium hydroxide. Pipette 15 ml potassium phosphate solution and 1.5 ml chloramine T solution into the flask in that order. After mixing and a reaction time of 1 min, add 3 ml barbituric acid/pyridine solution, make up to the mark with deionised water, and mix. The pH value of the solution should be about 6. After 20 min, measure at 570 nm against deionised water.

The reference curve is prepared from standard solutions of potassium cyanide treated in the same manner as the water sample.

Calculation

The use of an aliquot portion of the distillate diluted and, where necessary, made up to 25 ml is to be taken into account in the calculation.

1 mmol cyanide ions $\triangleq$ 26.0 mg CN^-.

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Barbituric acid/pyridine solution: Slurry 15 g Barbituric acid GR with a little deionised water, completely dissolve in 75 ml Pyridine GR, and treat with 15 ml Hydrochloric acid fuming min. 37% (about 1.19) GR. After cooling of the solution, make up to 250 ml with deionised water.

Chloramine T solution: Dissolve 1 g Chloramine T GR in 100 ml deionised water.

Cyanide standard solution: Dissolve 1.250 g Potassium cyanide GR in 0.2 mol/l sodium hydroxide to make 500 ml. 1 ml $\triangleq$ 1 mg CN^-.

The exact content of cyanide ions in the solution is ascertained by a titrimetric determination with silver nitrate solution using 5-(4-Dimethylaminobenzylidene)-rhodanine GR as indicator (see under 4.).

0.2 mol/l sodium hydroxide is used to make up the dilutions required for preparation of the reference curve.

The initial addition of 0.2 mol/l sodium hydroxide to the flask should always be in an amount adequate to avoid losses by escape of hydrocyanic acid.

Potassium dihydrogen phosphate solution: Dissolve 150 g Potassium dihydrogen phosphate GR in 850 ml deionised water.

Sodium hydroxide 0.2 mol/l: Make the contents of one ampoule of 0.1 mol/l Sodium hydroxide solution Titrisol concentrated solution for preparation of 1 litre of 0.1 N solution up to 500 ml with deionised water.

Reagents

Cat.No.		Packages
132	Barbituric acid GR	25 g, 100 g
2426	Chloramine T (trihydrate) GR	250 g, 1 kg
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
4873	Potassium dihydrogen phosphate GR	250 g, 1 kg, 5 kg
9959	Sodium hydroxide solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9140	Sodium hydroxide solution 0.2 mol/l	1 l
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
9728	Pyridine GR	500 ml, 1 l, 2½ l
317	Hydrochloric acid fuming min. 37% (about 1.19) GR	1 l, 2½ l

Rapid photometric analysis possible with Spectroquant® Cyanide
see Appendix

4. Titrimetric determination by means of silver nitrate solution using 5-(4-dimethylaminobenzylidene)rhodanine as indicator

Suitable for determination of cyanide ions in concentrations less than 5 mg/l CN^-.

Interferences

The interference of sulfide ions is excluded during the distillations under 1. and 2.

Procedure

Add 0.5 ml indicator solution to the distillate made up to 100 ml, or an aliquot portion thereof, and titrate with 0.01 mol/l silver nitrate solution until the colour changes to salmon red. Perform a blank test by titrating 100 ml deionised water under the same conditions until the same colour as the water sample.

Calculation

1 ml 0.01 mg/l CN^- silver nitrate solution ≙ 0.52 mg CN^-.

$$\text{mg/l } CN^- = \frac{(a-b) \times 0.52 \times 1000}{c}$$

a = ml of 0.01 mol/l silver nitrate consumed with the water sample
b = ml of 0.01 mol/l silver nitrate consumed in the blank test
c = ml of test water used in the distillation
The use of an aliquot portion of the distillate is to be taken into account.

1 mmol cyanide ions ≙ 26.0 mg CN^-

Reporting of results

The values are rounded off to 0.1 mg/l for less than 10 mg/l, and to 1 mg/l for 10 mg/l or higher.

Reagent preparations

Indicator solution: Dissolve 0.02 g 5-(4-Dimethylaminobenzylidene)rhodanine GR in 100 ml acetone. Stored protected from light the solution is stable for about 4 weeks.

Silver nitrate 0.01 mol/l: Make 100 ml 0.1 mol/l Silver nitrate solution up to 1000 ml with deionised water.

Reagents

Cat. No.		Packages
14	Acetone GR	1 l, 2½ l
3059	5-(4-Dimethylaminobenzylidene)rhodanine GR (reagent for silver)	5 g
9990	Silver nitrate solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9081	Silver nitrate solution 0.1 mol/l	1 l

Detergents, anionic

Suitable for determination of anionic detergents in concentrations from 0.20 to 1.50 mg/l referred to tetrapropylbenzenesulfonate (TBS).

Interferences and pre-treatment

The interference from sulfide ions is eliminated by addition of Perhydrol. In the case of simultaneous presence of cationic and anionic detergents, equivalent amounts come together, and escape detection with methylene blue.

Special constituents of the water sample can simulate too high values for anionic detergents as a result of formation of chloroform-soluble methylene blue compounds, or too low values through formation of compounds with the anionic detergents.

If the water is not tested immediately after sampling, it must be preserved, e.g., with a few ml of sulfuric acid or hydrogen sulfide-free water with a few ml mercury(II) chlorine solution. All the apparatus used must be thoroughly rinsed before the determination with alcoholic hydrochloric acid, double-distilled water and chloroform, in that order.

Procedure

First filter the water sample, discarding the first portion, and neutralise where necessary.

Introduce 100 ml of the water, or a smaller volume made up to 100 ml with double-distilled water, with a content between 20 and 150 μg anionic matter into a separating funnel, and add 10 ml alkaline sodium phosphate solution, 5 ml neutral methylene blue solution and 15 ml chloroform. In the case of heavily contaminated waters, start with a smaller volume and make up to 100 ml, in order to prevent formation of emulsions on shaking. Shake evenly for 1 min, and drain the clear chloroform phase into a second separating funnel containing 100 ml double-distilled water and 5 ml acid methylene blue solution. Shake again for 1 min, and then filter the chloroform layer through a cottonwool filter moistened with chloroform into a 50-ml volumetric flask. Repeat the extraction in alkaline and acid solution twice more with 10-ml portions of chloroform in each case.

Combine the chloroform extracts in the volumetric flask, and make up to the mark with the chloroform used to wash the cottonwool filter. Measure in 1-cm cells at 650 nm against a blank of 100 ml double-distilled water treated in the same manner.

The reference curve is prepared from standard solutions of tetrapropylbenzenesulfonate treated in the same manner as the water sample.

Reporting of results

The values are rounded off to 0.01 mg/l for a content of anionic detergents, referred to tetrapropybenzenesulfonate, from 0.02 to 0.1 mg/l, to 0.05 mg/l from 0.1 to 1.0 mg/l, and to 0.1 mg/l for more than 1.0 mg/l.
1 μmol tetrapropylbenzenesulfonate sodium ≙ 348 μg.

Reagent preparations

Methylene blue solution, neutral: Dissolve 0.35 g Methylene blue DAB 7 in double-distilled water to make 1000 ml.

The freshly prepared solution should be left to stand for at least 24 h before plotting the reference curve. The absorbance of the chloroform phase of the blank, measured against chloroform, may not exceed the value of 0.015 when 1-cm cells are used.

A new reference curve must be prepared for each new batch of methylene blue.

Methylene blue solution, acid: Dissolve 0.35 g Methylene blue DAB 7 in a 1000-ml volumetric flask with 500 ml double-distilled water, add 6.5 ml Sulfuric acid 95–97% (about 1.84) GR, and make up to the mark with double-distilled water.

The freshly prepared solution be left to stand for at least 24 h before plotting of the reference curve. The absorbance of the chloroform phase of the blank, measured against chloroform, may not exceed the value of 0.015 when 1-cm cells are used.

A new reference curve must be prepared for every new batch of methylene blue.

Sodium phosphate solution, alkaline: Dissolve 12.52 g di-Sodium hydrogen phosphate 2-hydrate GR in 500 ml double-distilled water. Adjust the solution to pH 10 with about 3 ml 0.5 mol/l sodium hydroxide, and make up to 1000 ml with double-distilled water. (With longer storage of the solution the pH value must be checked frequently, and adjusted if necessary.)

Mercury(II) chloride solution: Dissolve 10 mg Mercury(II) chloride GR in 1000 ml double-distilled water.

Hydrochloric acid, alcoholic: Mix 100 ml Ethanol absolute GR with 900 ml Hydrochloric acid min. 25% (about 1.125) GR.

Tetrapropylbenzenesulfonate standard solution:

Solution a: Make 20.0 ml Tetrapropylbenzenesulfonate solution 5% up to 1000 ml with double-distilled water.

Solution b: Dilute 50 ml Solution a to 1000 ml with double-distilled water.

Solution c: Dilute 50 ml Solution b to 1000 ml with double-distilled water. This solution is used for preparation of the reference curve. It contains 0.0025 g/l TBS.

The content of the Tetrapropylbenzenesulfonate solution 5% Standard for determination of anionic detergents is standardised to exactly 5% tetrapropylbenzenesulfonate (w/v) by the officially prescribed p-toluidine method (Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, 3. Auflage, H 23, page 4, or Verordnung über die Abbaubarkeit von Detergentien in Wasch- und Reinigungsmitteln dated 1. 12. 1962, Anlage to 2).

Reagents

Cat. No.		Packages
972	Ethanol absolute GR	1 l, 2½ l
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
2445	Chloroform GR	1 l, 2½ l
6040	Methylene blue DAB 7	100 g, 500 g
6580	di-Sodium hydrogen phosphate 2-hydrate GR	500 g, 1 kg, 5 kg
9957	Sodium hydroxide solution 0.5 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.5 N solution	1 amp.
9138	Sodium hydroxide solution 0.5 mol/l	1 l
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
4419	Mercury(II) chloride GR	50 g, 250 g, 1 kg
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
8202	Tetrapropylbenzenesulfonate solution 5% standard for determination of anionic detergents	250 ml

Detergents, cationic

Suitable for determination of cationic detergents in concentrations from 0.025 to 0.20 mg/l referred to cetyltrimethylammonium bromide (CTAB).

Pre-treatment

All the apparatus used should be rinsed out before the determination with chromosulfuric acid, double-distilled water and chloroform, in that order.

Procedure

Introduce 100 ml of the test water, or a smaller volume made up to 100 ml with double-distilled water, with a content of 2.5 to 20 μg cationic matter into a separating funnel, and add 10 ml citrate buffer solution, 5 ml 0.1 mol/l hydrochloric acid, 2 ml bromophenol blue solution and 15 ml chloroform. In the case of heavily contaminated water samples, start with a smaller volume made up to 100 ml with double-distilled water, in order to prevent the formation of emulsion on shaking. Shake evenly for 3 min, and then drain the chloroform layer into a 50-ml volumetric flask. Repeat the extraction with two 15-ml portions of chloroform. Combine the chloroform extracts in the volumetric flask, and make up to the mark with chloroform. Add a small spatula-tip of sodium sulfate anhydrous, allow to settle, and measure at 416 nm against chloroform.

The reference curve is prepared from standard solutions of cetyltrimethylammonium bromide treated in the same manner as the water sample.

Reporting of results

The values are rounded off to 0.05 mg/l for a content of cationic detergents, referred to cetyltrimethylammonium bromide, from 0.05 to 1.0 mg/l, and to 0.1 mg/l for more than 1.0 mg/l.

1 μmol cetyltrimethylammonium bromide (CTAB) ≙ 364 μg

Reagent preparations

Bromophenol blue solution, acid: Dissolve 0.150 g Bromophenol blue indicator in 200 ml 0.01 mol/l sodium hydroxide, and add 42 ml 0.1 mol/l hydrochloric acid. The solution should be left to stand for at least 3 days before use, but not stored longer than 14 days. A new reference curve must be prepared for each new batch of bromophenol blue.

Cetyltrimethylammonium bromide standard solution:

Solution a: Dissolve 1.00 g N-Cetyl-N,N,N-trimethylammonium bromide GR in double-distilled water with gentle warming. After cooling to room-temperature, make the solution up to 1000 ml with double-distilled water.

Solution b: Dilute 50 ml Solution b to 1000 ml with double-distilled water.

Solution c: Dilute 50 ml Solution b to 1000 ml with double-distilled water. This solution is used for preparation of the reference curve. The content of cationic detergent in

$$\text{g/l CTAB} = 0.0025 \times \frac{C}{100}$$

where C is the % content of cetyltrimethylammonium bromide (CTAB) in the respective reference substance. It is determined in accordance with the instructions on page 87.

Citrate buffer solution: Dissolve 21.00 g Citric acid GR in 200 ml 1 mol/l sodium hydroxide, and make the solution up to 1000 ml with double-distilled water. Dilute 309 ml of this solution to 1000 ml with 0.1 mol/l hydrochloric acid.

Reagents

Cat. No.		Packages
8122	Bromophenol blue indicator	5 g, 25 g
2342	N-Cetyl-N,N,N-trimethylammonium bromide GR	100 g, 1 kg
2445	Chloroform GR	1 l, 2½ l
2499	Chromosulfuric acid for cleaning glass vessels (LAB)	1 l, 2½ l
244	Citric acid 1-hydrate GR	500 g, 1 kg, 5 kg
6649	Sodium sulfate anhydrous GR	500 g, 1 kg, 5 kg
9961	Sodium hydroxide solution 0.01 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.01 N solution	1 amp.
9956	Sodium hydroxide solution 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9137	Sodium hydroxide solution 1 mol/l	1 l
9973	Hydrochloric acid 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9060	Hydrochloric acid 0.1 mol/l	1 l, 5 l

Determination of the degree of purity of the cationic reference substance

Suitable for the determination of cationic detergents in concentrations above 100 mg/l, the detergents being defined compounds as in the present case of N-cetyl-N,N,N-trimethylammonium bromide.

Procedure

Dissolve 2.00 g N-cetyl-N,N,N-trimethylammonium bromide in double-distilled water with gentle warming, and after cooling to room-temperature make up to 1000 ml with double-distilled water. Take 100 ml of the solution, and add 25.0 ml $^1/_{60}$ mol/l potassium dichromate with a pipette. Allow to stand for 2 h, and filter the resulting precipitate through a coarse membrane filter. Treat the clear filtrate with 5 g potassium iodide and 10 ml sulfuric acid, and titrate with 0.1 mol/l sodium thiosulfate until colourless, using zinc iodide-starch solution as indicator.

Treat 100 ml double-distilled water in the same manner in a blank test.

Calculation

$$\% \text{ content CTAB} = \frac{(a-b) \times A \times 0.333 \times 100}{c \times 1000}$$

a = ml of 0.1 mol/l sodium thiosulfate consumed in blank test
b = ml of 0.1 mol/l sodium thiosulfate consumed with the sample
c = weight, in g, of CTAB sample
A = equivalent weight of the cationic substance, in this case 364 for CTAB

Reporting of results

The values are rounded off to 0.5% CTAB.

Reagent preparation

Sulfuric acid (about 1.27): Carefully add 100 ml Sulfuric acid 95–97% (about 1.84) GR to 300 ml double-distilled water.

Reagents

Cat. No.		Packages
2342	N-Cetyl-N,N,N-trimethylammonium bromide GR	100 g, 1 kg
9928	Potassium dichromate solution $^1/_{60}$ mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
5043	Potassium iodide neutral GR	250 g, 1 kg, 2½ kg
9950	Sodium thiosulfate solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	1 l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
5445	Zinc iodide-starch solution GR	500 ml

Fluoride

Quantitative analysis

Photometrically after steam / acid distillation by means of lanthanum-alizarin complexone

Suitable for determination of fluoride ions in concentrations from 0.3 to 1.5 mg/l F^- (equivalent to 1.0 to 30 μg F^- per 100-ml flask).

Interferences and pre-treatment

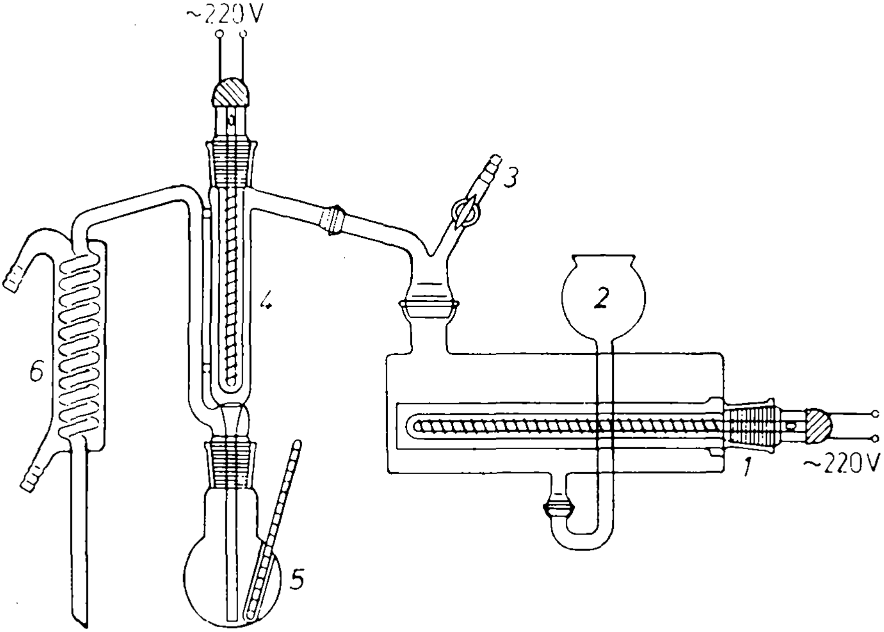
Evaporate 1000 ml of the water sample, or – depending on the fluoride content, which should not exceed 30 μg in the individual 1000-ml volumetric flasks during the distillation (see under Procedure) – a larger or smaller volume, in a platinum dish in an alkaline milieu. In the case of waters containing hydrogen carbonate the alkaline reactions sets in automatically on evaporation; in other cases add 1 mol/l sodium hydroxide dropwise.

In the case of presence of organic substances in the test water, ash the alkaline evaporation residue at not more than 450° C.

The interference of chloride ions is excluded by addition of an adequate amount of silver sulfate in the form of distillation sulfuric acid containing silver sulfate before the distillation. This requires a quantitative determination of the chloride ions in the water sample.

Procedure

A distillation apparatus according to *Seel* of pyrex glass is used for the steam/acid distillation (see illustration). The apparatus can be obtained from the firm Normag, Hofheim i. Ts., West Germany.



Distillation apparatus according to *Seel.* 1 Steam generator with rod immersion heater; 2 refilling funnel; 3 safety stopcock; 4 steam superheater (rod immersion heater); 5 sample flask (150 ml) with thermometer pocket (thermometer 0 to 200° C); spiral condenser (overall length about 30 cm, jacket length about 15 cm).

Transfer the evaporation residue or ash to the 150-ml sample flask with a maximum of 15 ml deionised water. If this amount of water does not suffice, it can be increased and then evaporated down to 15 ml again in the flask. Add 30 ml distillation sulfuric acid (the silver content is adequate to bind about 135 mg Cl^-; if necessary, add further silver sulfate), and connect the flask to the apparatus. Charge the steam generator with deionised water through the filling funnel until the level of the water is about 2 cm above the rod immersion heater. Under the outlet of the condenser place a 100-ml volumetric flask containing 3 ml 0.1 mol/l sodium hydroxide (for neutralisation of the acid distilling over it may be necessary to increase to 5 ml) and 0.5 ml 4-nitrophenol indicator, and marked at 40 ml. Keep five flasks similarly charged and marked in readiness.

Switch on the rod immersion heater. When the steam evolved reaches the steam super heater, switch this on also. The distillation temperature is normally 120 to 130° C.

After 40 ml of acid has distilled over into the first flask, substitute the other flasks in succession. A total of about 200 ml distillate will be collected.

Treat the alkaline distillate in the individual volumetric flasks with 0.05 mol/l sulfuric acid until the colour changes from yellow to colourless. Then add 50 ml lanthanum-alizarin complexone solution. It is advisable to use the same 50-ml pipette both for the determinations and for preparation of the reference curve, in order to guarantee a constant dropping of the acetonic colour solution. Make the flasks up to the mark with deionised water, allow 15 min reaction time at room-temperature, and measure at 600–620 nm against deionised water which has been treated in the same manner as the test water but without distillation.

The reference curve is prepared from standard solutions of sodium fluoride treated as described under Reagent preparations, Fluoride standard solution.

Calculation

$$\text{mg } F^-/\text{l test water} = \frac{S}{a}$$

S = sum of the $\mu g\ F^-$ found in volumetric flasks 1 to 5 (read from the reference curve)
a = ml of test water used
1 mmol fluoride ions ≙ 18.9984 mg F^-

Reporting of results

The values are rounded off to 0.01 mg/l.

Reagent preparations

Distillation sulfuric acid: The apparatus used in preparation of this reagent consists of a 1-litre round-bottomed flask with sidepocket for a thermometer reading to 200° C, and a ground-glass attachment through which an inlet tube passes almost to the bottom of the flask. The inlet tube is connected to a steam generator, and an outlet tube in the ground-glass attachment is connected to a spiral condenser via a ground-glass joint.

Introduce 500 ml of approx. 12 mol/l sulfuric acid (333 ml sulfuric acid 95–97% made up to 500 ml with deionised water) into the flask. Connect up the steam generator and the condenser, and heat the sulfuric acid to 120° to 130° C.

Pass in steam, and adjust the temperature to 150° C. Distill off and discard at least 500 ml at this temperature. The steam/acid distillation is complete once the temperature has risen to 171° C. The sulfuric acid remaining in the flask now has the original normality.

Heat 10 g silver sulfate and 10 ml sulfuric acid 95–97% in a porcelain dish until SO_2 vapours are evolved, and then for a further 10 min. After cooling, combine the solution with the 500 ml 12 mol/l sulfuric acid in a beaker, and heat with continuous stirring until the solution is clear.

Store the distillation sulfuric acid in a dark bottle.

Fluoride standard solution: Dissolve 2.210 g Sodium fluoride GR in deionised water, and make up to 1000 ml. 1 ml ≙ 1 mg F. The dilutions necessary for plotting of the reference curve are freshly prepared from this solution as required. 100-ml volumetric flasks are treated with 3 ml 0.1 mol/l sodium hydroxide and 0.5 ml 4-nitrophenol indicator solution, and then further treated in the same manner as the alkaline distillate of the test water.

Lanthanum-alizarin complexone solution:

Solution a) Alizarin complexone solution 0.004 M: Dissolve 1.6854 g Alizarin-3-methylamine-N,N-diacetic acid (dihydrate) for spectrophotometric determination of fluoride in 20 ml of a 0.5 M solution of sodium acetate (dissolve 41 g Sodium acetate anhydrous GR in deionised water, and make up to 1000 ml) with warming, and after cooling make up to 1000 ml with deionised water.

Solution b) Lanthanum nitrate solution 0.004 M: Dissolve 1.7322 g Lanthanum nitrate GR in deionised water, and make up to 1000 ml.

Solution c) Acetate buffer solution (pH 4.4): Mix 630 ml 0.5 M acetic acid (29 ml Acetic acid glacial min. 96% GR and 971 ml deionised water) and 370 ml 0.5 M sodium acetate solution (prepared as under Solution a). Adjust the solution to a pH of exactly 4.4 using a pH-meter.

To prepare the lanthanum-alizarin complexone solution, introduce 50 ml Solution a, 50 ml Solution b, 80 ml Solution c and 500 ml acetone into a 1000-ml volumetric flask, and make up to the mark with deionised water. The pH of this solution should be 5.6–5.8, and must be adjusted to this value where necessary. Stored in a refrigerator the solution is stable for at least 2 to 3 months.

4-Nitrophenol indicator solution: Dissolve 0.2 g 4-Nitrophenol indicator in deionised water, and make up to 100 ml. Colour change from yellow (alkaline) to colourless (acid) at pH 5.4–7.5.

Reagents

Cat. No.		Packages
14	Acetone GR	1 l, 2½ l
1010	Alizarin-3-methylamine-N,N-diacetic acid (dihydrate) for spectrophotometric determination of fluoride	1 g, 5 g
62	Acetic acid glacial main. 96% (about 1.06) GR	1 l, 2½ l
5326	Lanthanum nitrate GR	25 g, 100 g
6268	Sodium acetate anhydrous GR	250 g, 1 kg, 5 kg
6449	Sodium fluoride GR	100 g, 250 g, 1 kg
9959	Sodium hydroxide solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9141	Sodium hydroxide solution 0.1 mol/l	1 l, 5 l, 50 l
9956	Sodium hydroxide solution 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9137	Sodium hydroxide solution 1 mol/l	1 l, 50 l
6798	4-Nitrophenol indicator	25 g, 100 g
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
9984	Sulfuric acid 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9074	Sulfuric acid 0.05 mol/l	1 l, 5 l, 50 l
1509	Silver sulfate GR	25 g, 100 g

Hardness

Rapid determination possible with Merckoquant® Test Strips and with Aquamerck® Reagent Kits

see Appendix

1. Determination of the total hardness (sum of alkaline earths)

Total hardness of a water: Sum of the alkaline earths (magnesium, calcium, strontium and barium ions) bound as carbonates, sulfates, chlorides, nitrates and phosphates, expressed in mmol/l or in degrees of German hardness (°d).

1.1 Complexometric determination with Titriplex® solutions A, B and C, and Indicator buffer tablets

Interferences and pre-treatment

Alkaline waters are adjusted to pH 6–8 with 1 mol/l hydrochloric acid. In the case of high phosphate content it is advisable to remove the former with a strongly basic ion exchanger. The exchanger should first be converted into the chloride form by treating in a column with sodium chloride solution (2–3 litres per 1 litre of ion exchanger), and then washing until free from chloride with deionised water.

Iron, manganese and copper ions interfere.

Iron and manganese ions may be masked with triethanolamine. In the presence of manganese ions it is also advisable to add a little hydroxylammonium chloride or ascorbic acid, since manganese(III) salt can oxidise the indicator dyestuff.

If more than 1 mg/l Fe is present, making the colour change difficult to detect, it is expedient to proceed as follows, in place of the titration method with indicator buffer tablets:

Add 2 ml triethanolamine to the test water, make strongly ammoniacal, add a spatula-tip of methylthymol blue indicator triturate, and titrate with one of the Titriplex solutions.

At extremely high iron concentrations a back-titration is unavoidable:

Add triethanolamine and a measured volume of Titriplex solution to the test water, and make ammoniacal. The intensely brown-coloured solution becomes colourless. Then back-titrate the excess Titriplex solution with standardised calcium chloride solution and methylthymol blue indicator triturate.

Waters containing copper are pre-treated by adding the following reagents in the order given: 1–2 ml ammonia solution, a knife-tip of potassium cyanide, one indicator buffer tablet, and after the latter has dissolved, 1–2 drops formaldehyde solution. Then titrate.

1.1.1 Complexometric determination with Titriplex® solution A

(Raw water, medium-hard and hard water)

Dissolve 1 indicator buffer tablet in 100 ml of the water sample. Add 1–2 ml ammonia solution, and immediately titrate with Titriplex solution A until the colour changes from red via grey to green.

When 100 ml water is used, 1 ml of Titriplex solution A consumed is equivalent to 1.0 mmol/l or 2.0 meq/l or 5.6° d.

1.1.2 Complexometric determination with Titriplex solution B

(Soft, pre-softened or softened water)

Dissolve 1 indicator buffer tablet in 100 ml of the test water. Add 1–2 ml ammonia solution, and titrate immediately with Titriplex solution B until the colour changes from red via grey to green.

When 100 ml water is used, 1 ml of Titriplex B solution consumed is equivalent to 0.18 mmol/l or 0.36 meq/l or 1.0 °d.

In the case of very soft waters, there is no objection to diluting the Titriplex solution B further with freshly distilled water as required, e.g., ten-fold or twenty-fold. The results of the titration are converted to mmol/l or meq/l or °d according to the dilution.

In order to keep the titre constant, the greatly diluted Titriplex solutions are stored in polyethylene bottles.

1.1.3 Complexometric determination with Titriplex® solution C in an H DIN 12812 burette

Fill the 50 DIN 12685 mixing cylinder of an H DIN 12812 burette with the test water up to the 40-ml mark, and dissolve an indicator buffer tablet in the water. Add 1–2 ml ammonia solution, and then immediately drip in Titriplex solution C from the burette which has been filled to the 0-mark, until the colour changes from red via a grey shade to green. In the case of waters with 10–20 °d, use 20 ml test water and 20 ml deionised water, and in the case of waters with more than 20 °d, 10 ml test water and 30 ml deionised water.

The total hardness is read directly from the burette according to the level of Titriplex solution C. In the case of waters with over 10 °d multiply the value read by 2 or 4 depending on the amount of water used.

Rapid testing of softened water with indicator buffer tablets

Pre-treatment

When sulfides are present, waters almost free from hardness may exhibit a green shade without the water being completely softened. This interference may be eliminated by acidifying and boiling, thereby expelling the hydrogen sulfide. The rapid testing can then be carried out after neutralisation with sodium hydroxide solution.

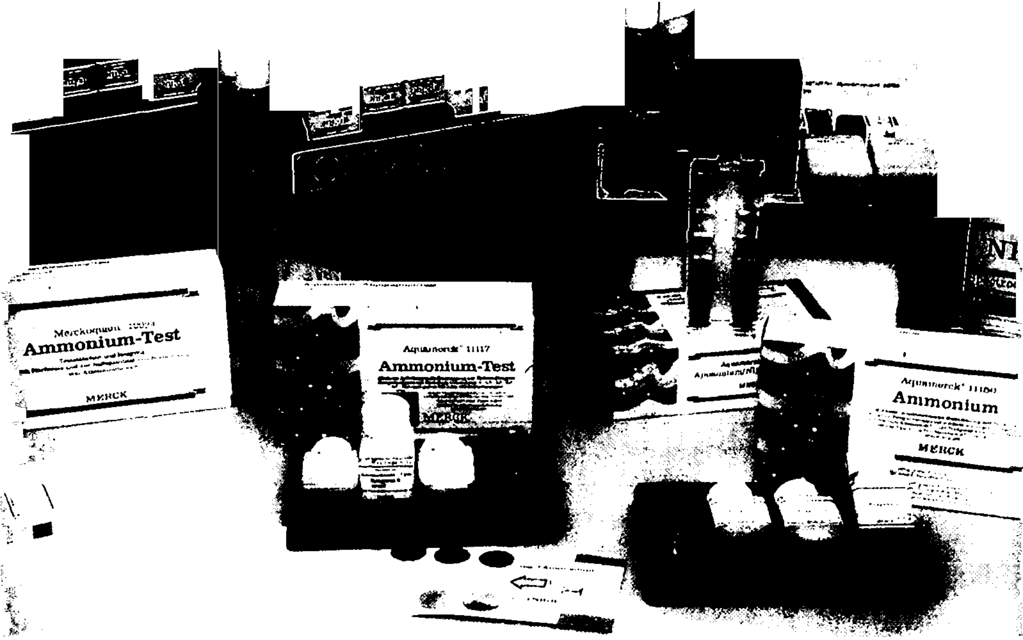
Procedure

To detect whether waters are completely or practically completely softened, dissolve 1 indicator buffer tablet in 100 ml of the test water, and add 1 ml ammonia solution.

Green colouration (with greyish undertone)	0.0 °d
Grey to greyish-violet mixed colour	>0.01 °d
Pink colouration	0.05 °d

When copper is present, treat 100 ml of the water with 1 ml ammonia solution and a knife-tip of potassium cyanide before adding the indicator buffer tablet. After the tablet has dissolved, add 1–2 drops formaldehyde solution, and evaluate the colour.

If a markedly red colour develops, the hardness is greater than 0.05 °d. In such cases it is necessary to carry out an exact determination by titrating with Titriplex


Merckoquant
Ammonium-Test
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Ammonium
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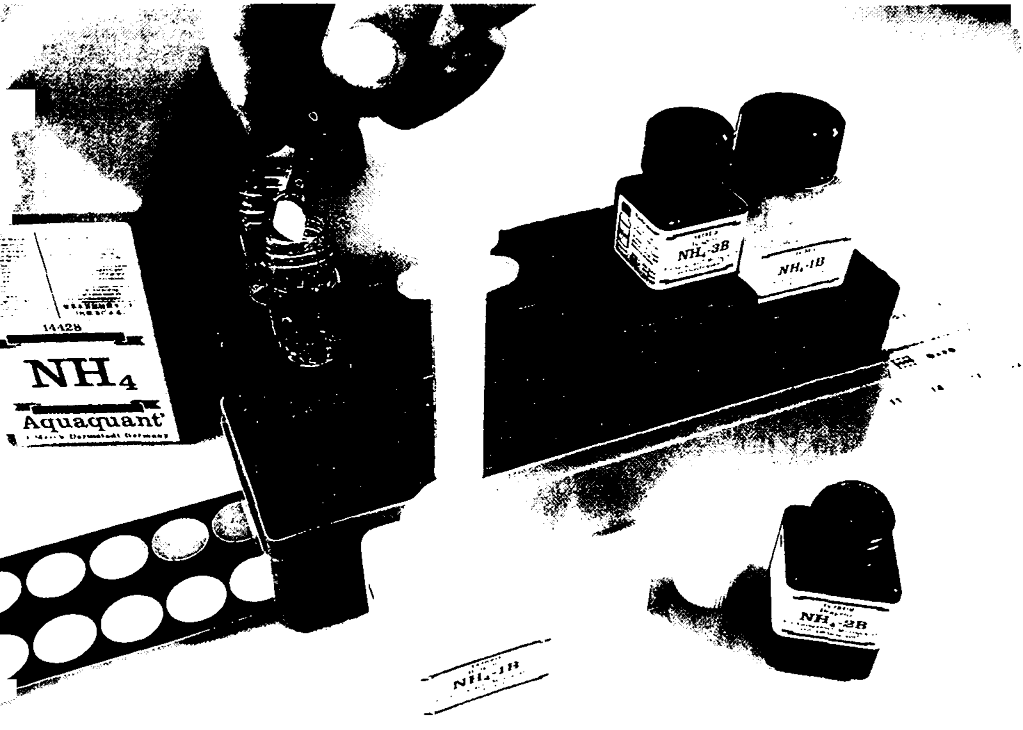
14428
NH4
Aquaquant
NH4-3B
NH4-1B
NH4-2B
NH4-1B

solutions A, B or C in accordance with one of the methods given in the preceding pages.

Evaluation of the hardness in terms of German degrees of hardness

0– 4 °d	very soft
4– 8 °d	soft
8–18 °d	medium-hard
18–30 °d	hard
>30 °d	very hard

Conversion table

	Alkaline earth ions mmol/l	Alkaline earth ions meq/l	German degree °d	ppm $CaCO_3$	Engl. degree °e	French degree °f
1 mmol/l alkaline earth ions	1.00	2.00	5.60	100.0	7.02	10.00
1 meq/l alkaline earth ions	0.50	1.00	2.80	50.0	3.51	5.00
1 German degree	0.18	0.357	1.00	17.8	1.25	1.78
1 ppm $CaCO_3$	0.01	0.020	0.056	1.00	0.0702	0.100
1 English degree	0.14	0.285	0.798	14.3	1.00	1.43
1 French degree	0.10	0.200	0.560	10.0	0.702	1.00

In commercial transactions in West Germany only the statutory units of measurement (SI Units) may be used according to the Gesetz über Einheiten im Messwesen dated 2nd July 1969. Of the units listed above, only the "mmol/l" is an SI unit.

Reporting of results

The values are rounded off to 0.01 mmol/l at a hardness of less than 1 mmol/l, to 0.05 mmol/l from 1 to 5 mmol/l, to 0.1 mmol/l from 5 to 10 mmol/l, to 0.5 mmol/l from 10 to 20 mmol/l, and to 1 mmol/l for more than 20 mmol/l. The equivalents hold good for reporting of the results in meq/l or °d.

Reagent preparations

Calcium chloride solution 0.005 mol/l: Dissolve 0.500 g Calcium carbonate precipitated GR volumetric standard, dried at 105° C, in 110 ml 0.1 mol/l hydrochloric acid. Heat the solution to boiling, cool, and make up to 1000 ml with deionised water.

Methylthymol blue indicator triturate: Triturate 1 g Methylthymol blue sodium salt with 100 g Potassium nitrate GR.

Sodium chloride solution: Dissolve 5 g Sodium chloride GR in deionised water, and make up to 100 ml.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
127	L(+) Ascorbic acid GR	100 g, 250 g, 1 kg
2060	Calcium carbonate precipitated GR volumetric standard	100 g
4003	Formaldehyde solution 35% stabilised with about 10% methanol GR	1 l, 5 l
4616	Hydroxylammonium chloride GR	100 g, 250 g, 1 kg
8430	Indicator buffer tablets for determination of water hardness with Titriplex® solutions	500 tabl., 1000 tabl.
5239	Ion exchanger Merck Lewatit® M 5080 G3 GR 0.1–0.25 mm (60–150 mesh ASTM) strong base anion exchanger type I with colour indicator Cl^- form	100 ml, 500 ml
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
5063	Potassium nitrate GR	500 g, 1 kg, 5 kg
6084	Methylthymol blue sodium salt metal (pM) indicator	1 g, 5 g
6404	Sodium chloride cryst. GR	500 g, 1 kg, 5 kg
5594	Sodium hydroxide solution 20% GR	1 l
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
9973	Hydrochloric acid 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9060	Hydrochloric acid 0.1 mol/l	1 l, 5 l, 50 l
9970	Hydrochloric acid 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9057	Hydrochloric acid 1 mol/l	1 l, 5 l, 50 l
	Titriplex® solutions for determination of water hardness:	
8419	Solution A 1 ml ≙ 56 mg/l CaO (≙ 7 British degrees of hardness) if 100 ml of water are used	1 l

8420	Solution B 1 ml ≙ 10 mg/l CaO (≙ 1.25 British degrees of hardness) if 100 ml of water are used	1 l, 5 l
8429	Solution C (with measuring tube H DIN 12812) 2.3 ml ≙ 123 mg/l CaO (≙ 15.4 British degrees of hardness) if 40 ml of water are used	1 l
	Titrisol® for determination of water hardness:	
9894	for preparation of 1 litre of Titriplex® solution A 1 ml ≙ 56 mg/l CaO (≙ 7 British degrees of hardness) if 100 ml of water are used	1 amp.
9895	for preparation of 1 litre of Titriplex® solution B 1 ml ≙ 10 mg/l CaO (≙ 1.25 British degrees of hardness) if 100 ml of water are used	1 amp.
8379	Triethanolamine GR	250 ml, 1 l

2. Determination of carbonate hardness

Carbonate hardness signifies the total hardness induced by the proportion of the alkaline earth ions which is equivalent to the carbonate and hydrogen carbonate ions contained in the water and to the hydroxyl ions resulting from their hydrolysis.

If the water contains more equivalents of carbonate and hydrogen carbonate ions than of alkaline earth ions, then a higher value is found for the cabonate hardness than for the total hardness. In this case the total hardness is reported as carbonate hardness.

Procedure

Treat 100 ml of the water sample with 3 drops of phenolphthalein solution and, if a red colour is produced, with 0.1 N hydrochloric or sulfuric acid until the solution becomes colourless. Add 2 drops of mixed indicator solution, and titrate the sample further until the colour changes from green via greyish-green to violet. If no red colour is produced on addition of phenolphthalein solution, add the mixed indicator solution immediately, and titrate until the colour change to violet.

Calculation

Number of ml of 0.1 N acid consumed up to colour change of phenolphthalein = p-value in meq/l

Total number of ml of 0.1 N acid consumed up to colour change of the mixed indicator = m-value in meq/l

The carbonate hardness is calculated from the p- and m-values as follows:
a) $2p \leqq m$; carbonate hardness: $x = m$
b) $2p > m$; $> p$; carbonate hardness: $x = 2(m - p)$
c) $p = m$; carbonate hardness: $x = 0$

If the value for carbonate hardness is higher than that for the total hardness, the total hardness is reported as carbonate hardness.

For conversion of the values from meq/l to mmol/l or °d, see under 1.

Reporting of results

As under 1.

Reagent preparations

Mixed indicator solution:

Solution a: 600 mg Methyl red sodium salt indicator and 100 ml deionised water.
Solution b: 400 mg Methylene blue B and 400 ml deionised water.
Mix the two solutions with one another.

Reagents

Cat. No.		Packages
1283	Methylene blue B	25 g, 100 g
6078	Methyl red sodium salt indicator	25 g, 100 g
7227	Phenolphthalein solution 1% in ethanol indicator	250 ml, 1 l
9973	Hydrochloric acid 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9060	Hydrochloric acid 0.1 mol/l	1 l, 5 l, 50 l
9984	Sulfuric acid 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9040	Sulfuric acid 0.05 mol/l	1 l, 5 l

3. Determination of the non-carbonate hardness

The non-carbonate hardness is calculated by subtracting carbonate hardness from total hardness.

Hydrazine

Qualitative analysis

Treat 50 ml of the water sample with 10 ml 4-dimethylaminobenzaldehyde solution. In the presence of hydrazine a yellow to orange-red colour is produced depending on the concentration.

Reagent preparation

See Quantitative analysis

Rapid determination possible with Aquamerck®, Aquaquant® and Microquant® Reagent Kits

See Appendix.

Quantitative analysis

Photometrically by means of 4-dimethylaminobenzaldehyde

Suitable for determination of hydrazine in concentrations between 0.005 and about 1 mg/l.

Interferences and pre-treatment

No interference is caused by foreign substances to be found in boiler feed waters and condensates such as heavy metal ions, neutral salts, ammonia and phosphate ions.
Turbid waters are filtered through a filter paper until clear before determination.
The water sample should exhibit a neutral reaction, and be cooled to room-temperature.

Procedure

Treat 50 ml of the water sample, or a smaller volume made up to 50 ml with hydrazine-free deionised water according to the hydrazine concentrations with 10 ml

4-dimethylaminobenzaldehyde solution or 10 ml Aquamerck hydrazine reagent. After 10 min reaction time, measure at 450 nm against a blank treated in the same manner.

The reference curve is prepared from standard solutions of hydrazinium sulfate treated in the same manner as the water sample.

Calculation

Any dilution of the water sample to 50 ml starting volume is to be taken into account in the calculation.

Reporting of Results

The values are rounded off to 0.001 mg hydrazine/l for 0.01 to 0.1 mg/l, to 0.01 mg hydrazine/l for 0.1 to 10 mg/l, and to 0.1 mg hydrazine/l for more than 10 mg/l.

Reagent preparations

4-Dimethylaminobenzaldehyde solution: Dissolve 2 g 4-Dimethylaminobenzaldehyde GR in 0.5 mol/l Sulfuric acid to make 100 ml.

Hydrazine standard solution: Dissolve 4.100 g Hydrazinum sulfate GR in deionised water to make 1000 ml.

1 ml ≙ 1 mg hydrazine.

The dilutions necessary for plotting the reference curve are freshly prepared from this solution before use.

Reagents

Cat. No.		Packages
3058	4-Dimethylaminobenzaldehyde GR	25 g, 100 g, 1 kg
4603	Hydrazinium sulfate GR	100 g, 500 g
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
9072	Sulfuric acid 0.5 mol/l	1 l, 5 l
9981	Sulfuric acid 0.5 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.

Rapid photometric analysis possible with Spectroquant® Hydrazine

see Appendix

Hydrogen sulfide

Qualitative analysis

1. Hydrogen sulfide may be recognised from its characteristic odour, which disappears on addition of cadmium carbonate.

2. Lead acetate paper is hung in a closed flask in the atmosphere above the test water. Depending on concentration the filter paper takes on a brown colour immediately or on longer standing, as a result of the formation of lead sulfide.

Reagents

Cat. No.		Packages
9511	Lead(II) acetate paper (100-strip booklet)	1 pack
2009	Cadmium carbonate extra pure	500 g

Rapid determination possible with Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative analysis

Titrimetrically after precipitation as cadmium sulfide

Suitable for determination of hydrogen sulfide in concentrations greater than 2 mg/l H_2S.

Interferences

Hydrosulfide and sulfide ions are co-determined.

Procedure

The apparatus required consists of a distillation flask with separating funnel attached. The flask is connected to a bulb-tube washer, and provided with a gas inlet tube. The latter is connected to a cylinder of nitrogen via a gas-washing bottle. The bulb-tube washer contains 20–30 ml cadmium acetate solution, and the gas-washing bottle about 100 ml nitrogen-purifying solution. Free the apparatus from oxygen to a large extent by passing nitrogen through, then introduce 200 ml of the water sample, or a larger volume according to concentration, through the separating funnel. Expel the hydrogen sulfide it contains into the bulb-tube washer by passing in nitrogen for several hours. After 5 hours, filter the cadmium sulfide formed through asbestos, wash with deionised water, dissolve in a conical flask in excess 0.005 mol/l iodine (50 ml or more), and acidify with phosphoric acid. After 20 min, back-titrate the excess iodine with 0.01 mol/l sodium thiosulfate, using zinc iodine-starch solution as indicator.

Calculation

1 ml 0.005 mol/l iodine solution ≙ 0.1704 mg H_2S

$$\text{mg/l } H_2S = \frac{(a-b) \times 0.1704 \times 1000}{c}$$

a = ml of 0.005 mol/l iodine added
b = ml of 0.01 mol/l sodium thiosulfate consumed
c = ml of test water used

1 mmol hydrogen sulfide ≙ 34.08 H_2S

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Cadmium acetate solution: Dissolve 5 g Cadmium acetate GR in 30 ml Acetic acid glacial min. 96% (about 1.06) GR and 65 ml deionised water.

Iodine 0.005 mol/l: Dilute 100 ml 0.05 mol/l iodine to 1000 ml with boiled deionised water as required.

Sodium thiosulfate solution 0.01 mol: Dilute 100 ml of 0.1 mol/l sodium thiosulfate solution to 1000 ml with boiled deionised water as required.

Phosphoric acid: Dilute 124 ml ortho-Phosphoric acid min. 85% (about 1.71) GR with 500 ml deionised water.

Nitrogen-purifying solution: Dissolve 5 g Mercury(II) chloride GR in potassium permanganate solution (2 g Potassium permanganate GR dissolved in deionised water to make 100 ml) to make 100 ml.

Reagents

Cat. No.		Packages
1560	Asbestos for Gooch crucibles (LAB)	100 g, 1 kg
2003	Cadmium acetate GR	100 g, 500 g
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
9910	Iodine solution 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9099	Iodine solution 0.05 mol/l	1 l
5082	Potassium permanganate GR	250 g, 1 kg
9950	Sodium thiosulfate solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	1 l
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
4419	Mercury(II) chloride GR	50 g, 250 g, 1 kg
823 314	Nitrogen	0.44 l, 50 l
5445	Zinc iodide-starch solution GR	500 ml

Rapid photometric analysis possible with Spectroquant® Hydrogen Sulfide

see Appendix

Iron

Qualitative analysis

Iron(II) ions: Treat 100 ml of the water sample with 0.5 ml 0.05 mol/l sulfuric acid and 1 ml 2,2'-bipyridine solution. A pink to red colour develops on standing depending on the iron content.

Iron(III) ions: Treat 100 ml of the water sample with 3 ml hydrochloric acid (about 1.125) and 3 ml potassium thiocyanate solution. Iron(III) ions are indicated by a brownish-red colour.

Iron(II) and iron(III) ions together: Boil 100 ml of the water sample with 0.5 ml hydrogen peroxide solution and 3 ml hydrochloric acid (about 1.125), and add 3 ml potassium thiocyanate solution. In the presence of iron ions a brownish-red colour is produced.

Reagent preparations

2,2'-Bipyridine solution: Dissolve 0.4 g 2,2'-Bipyridine GR in deionised water, and make up to 100 ml.

Potassium thiocyanate solution: Dissolve 10 g Potassium thiocyanate GR in deionised water, and make up to 100 ml.

Hydrogen peroxide solution (3%): Dilute 10 ml Perhydrol 30 % H_2O_2 GR with 90 ml deionised water as required.

Reagents

Cat. No.		Packages
3098	2,2'-Bipyridine (α, α'-dipyridyl) GR [reagent for iron(II) and molybdenum]	5 g, 25 g
5125	Potassium thiocyanate GR	250 g, 1 kg, 5 kg

7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
9984	Sulfuric acid 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre 0.1 N solution	1 amp.
9074	Sulfuric acid 0.05 mol/l	1 l, 5 l

Rapid determination possible with Merckoquant® Test Strips and with Aquamerck®, Aquaquant® and Microquant® Reagent Kits
see Appendix

Quantitative analysis

Photometrically by means of 1,10-phenanthrolinium chloride

Suitable for determination of iron ions in concentrations from 0.01 to 4 mg/l, determined as iron(II) ions.

Interferences and pre-treatment

When hydroxylammonium chloride is used as reducing agent copper ions interfere in concentrations above 20 mg/l, and when ascorbic acid is used they interfere in concentrations above 2 mg/l.

Nickel and zinc ions interfere in concentrations above 10 mg/l when either hydroxylammonium chloride or ascorbic acid is used.

Interference from orthophosphate ions in concentrations above 100 mg/l PO_4^{3-} is to be observed with absorbic acid as reducing agent.
Cyanide ions interfere in amounts above 2 mg/l CN^-.

Complex iron compounds are decomposed by oxidation with sulfuric acid (about 1.84), the solution being evaporated until sulfur trioxide vapours begin to evolve.

Procedure

Introduce 2 ml 1 mol/l sulfuric acid into a volumetric flask, and make up to the mark with clear test water. In the case of turbid water, filter into the flask through a plaited filter. Close the flask, and carry out the analysis within the next two hours.

Treat 50 ml of the acidified water sample in a conical flask with 2 ml ammonium acetate-glacial acetic acid solution and 1 ml hydroxylammonium chloride solution. In the presence of orthophosphate ions it is advisable to add 2 ml sodium acetate-glacial acetic acid solution and 1 ml ascorbic acid solution instead. In both cases the pH value should be between 3.5–5.5, and where possible 4.5. Mix well, add 2 ml 1,10-phenanthrolinium chloride solution, and allow to stand for 15 min in the dark. Then measure at 492 nm or 508 nm against a blank prepared with deionised water.

The reference curve is prepared from standard solutions of iron or dilution solutions of Iron standard solution Titrisol treated in the same manner as the test water. The volume of the sulfuric acid added at the beginning of the analysis is to be taken into account.

If the total iron of a turbid test water is to be determined, the residue remaining on the plaited filter is brought into solution with hydrochloric acid, and the pH adjusted to 4.5 with sodium hydroxide solution before the iron is determined.

Reporting of results

The values are rounded off to 0.001 mg/l for an iron content from 0.01 to 0.1 mg/l, to 0.01 mg/l for 0.1 to 10 mg/l and to 0.1 mg/l for more than 10 mg/l.
1 mmol iron ≙ 55.85 mg Fe
1 meq iron(II) ions ≙ 27.93 mg Fe^{2+}
1 meq iron(III) ions ≙ 18.62 Fe^{3+}

Reagent preparations

Ammonium acetate-glacial acetic acid solution: Dissolve 40 g Ammonium acetate GR and 50 ml Acetic acid glacial min. 96% (about 1.06) GR in deionised water, and make up to 100 ml.

Ascorbic acid solution: Dissolve 10 g Ascorbic acid GR in deionised water to make 100 ml. (Prepare the solution fresh daily!)

Iron standard solution: Moisten 500 mg Iron reduced GR in a 500-ml volumetric flask with a little deionised water, and dissolve in 5 ml Hydrochloric acid min. 25% (about 1.125) GR. After cooling, make up to the mark with deionised water. 1 ml ≙ 1 mg Fe.

Iron standard solution: Make up the contents of one ampoule of Iron standard solution Titrisol to 1000 ml with deionised water.
1 ml ≙ 1 mg Fe.
The dilutions necessary for plotting the reference curve are freshly prepared from the iron standard solution as required.

Hydroxylammonium chloride solution: Dissolve 20 g Hydroxylammonium chloride GR in 100 ml deionised water. (The solution is stable for about 1 week).

Sodium acetate-glacial acetic acid solution: Dissolve 16.5 g Sodium acetate cryst. GR and 11.5 ml Acetic acid glacial min. 96% (about 1.06) GR in deionised water, and make up to 100 ml.

Sodium hydroxide 2 mol/l: Make the contents of one ampoule of 1 mol/l Sodium hydroxide Titrisol concentrated solution for preparation of 1 litre of 1 N solution up to 500 ml with deionised water.

1,10-Phenanthrolinium chloride solution: Dissolve 0.5 g 1,10-Phenanthrolinium chloride GR in 100 ml deionised water. (The solution is stable for about 1 week).

Sulfuric acid 1 mol/l: Make the contents of one ampoule of 0.5 mol/l Sulfuric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution up to 500 ml with deionised water.

Reagents

Cat. No.		Packages
9531	Acilit® indicator strips pH 0–6.0 non-bleeding graduated in 0.5 pH units	1 pack
1116	Ammonium acetate GR	500 g, 1 kg, 5 kg
127	L(+) Ascorbic acid GR	100 g, 250 g, 1 kg
3819	Iron reduced GR	100 g, 1 kg
9972	Iron standard solution Titrisol® 1.000 g ± 0.002 Fe ($FeCl_3$ in dil. HCl)	1 amp.
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l
4616	Hydroxylammonium chloride GR	100 g, 250 g, 1 kg
6267	Sodium acetate cryst. GR indifferent to potassium permanganate	500 g, 1 kg, 5 kg
9956	Sodium hydroxide solution 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9136	Sodium hydroxide solution 2 mol/l	1 l
7223	1,10-Phenanthrolinium chloride (monohydrate) GR and redox indicator [reagent for iron(II)]	5 g, 10 g, 100 g
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l
9981	Sulfuric acid 0.5 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
731	Sulfuric acid 95–97% (about 1.84) GR	1 l

Rapid photometric analysis possible with Spectroquant® Iron
see Appendix

Lead

Qualitative analysis

Treat the test water successively with a few drops of potassium sodium tartrate solution, with sodium hydroxide solution to marked alkalinity, and with a few drops of potassium cyanide solution. On addition of a few ml of a freshly prepared solution of hydrogen sulfide a more or less intense yellow to greyish-brown turbidity is produced as a result of colloidal lead sulfide when lead ions are present.

Reagent preparations

Potassium cyanide solution: Dissolve 10 g Potassium cyanide GR in deionised water, and make up to 100 ml.

Potassium sodium tartrate solution: Dissolve 50 g Potassium sodium tartrate GR in deionised water, and make up to 100 ml.

Sodium hydroxide solution: Dissolve 33 g Sodium hydroxide pellets GR in deionised water to make 100 ml.

Hydrogen sulfide solution: Pass hydrogen sulfide gas into deionised water until saturated.

Reagents

Cat. No.		Packages
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
8087	Potassium sodium tartrate GR	500 g, 1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
823 310	Hydrogen sulfide	0.44 l
7996	Sulfidogen® (sulfur-paraffin) for generation of hydrogen sulfide	500 g

Quantitative analysis

1. Photometrically with dithizone for low concentrations

Suitable for determination of lead ions in concentrations from 0.001 to 0.1 mg Pb^{2+} absolute or 0.02–2.0 mg/l Pb^{2+}.

Interferences and pre-treatment

Bismuth, indium and thallium ions interfere in the determination. The other cations are masked by potassium cyanide (see under Procedure); they only interfere at concentrations above 100 mg/l.

Phosphate ions in concentrations up to 100 mg/l do not interfere.

Lead compounds which are only slightly soluble, such as lead sulfate and lead phosphate, are brought into solution by addition of potassium sodium tartrate (see under Procedure).

In the presence of sulfides the water sample is evaporated to dryness with a few drops of nitric acid, moistened again with nitric acid and evaporated to dryness. The residue is dissolved in 50 ml deionised water and 2 ml potassium sodium tartrate solution, with warming.

The interference of oxidising substances and of iron(III) ions (the latter not interfering at less than 20 mg/l) is eliminated by addition of hydrazinium chloride solution (see under Procedure).

Organic lead compounds and other organic substances (potassium permanganate consumption above 25 mg/l) are decomposed by evaporation with sulfuric acid and a few drops of nitric acid.

Procedure

Pre-treat the water sample as necessary. Depending on the lead content, which should not exceed 100 μg in the volume of sample taken, acidify 50–250 ml with hydrochloric acid min. 25% (about 1.125), boil for about 5 min to remove the carbon dioxide, neutralise with ammonia solution, and transfer completely to a separating funnel. For each 50 ml of the water add 5 ml Solution I, 5 ml Solution II, and a total of 25 ml dithizone solution. Shake for 5 min, and then drain the chloroform phase after settling through a dry filter paper into a glass-stoppered vessel. Measure in 1-cm cells at 515 nm against a blank of the same volume of deionised water in place of the water sample treated in the same manner.

The reference curve is prepared from standard solutions of lead nitrate or dilution solutions of Lead standard Titrisol treated in the same manner as the water sample.

Calculation

The lead ion content of the sample is calculated in mg Pb^{2+}/l from the amount of water used and the absolute amount of lead determined from the calibration curve.
1 mmol lead ions ≙ 207.2 mg Pb^{2+}
1 mg Pb^{+} ≙ 1.077 mg PbO

Reporting of results

The values are rounded off to 0.001 mg/l for less than 0.02 mg/l, to 0.01 mg/l from 0.02 to 0.2 mg/l, to 0.05 mg/l from 0.2 to 2 mg/l, and to 0.1 mg/l for more than 2 mg/l.

Reagent preparations

Lead standard solution: Add 1 ml Nitric acid min. 65% (about 1.40) tested by the dithizone method GR to 1.599 g Lead(II) nitrate GR (powdered and dried at 100° C), and make up to 1000 ml with double-distilled water. 1 ml ≙ 1 mg Pb^{2+}.

Lead standard solution: Make the contents of one ampoule of Lead standard solution Titrisol up to 1000 ml with double-distilled water. 1 ml ≙ 1 mg Pb^{2+}.

The dilution solutions necessary for plotting the reference curve are always freshly prepared with double-distilled water from the lead standard solution as required.

Dithizone solution: Dissolve 15 mg Dithizone (1,5-diphenylthiocarbazone) GR in 1000 ml Chloroform GR (for determinations with dithizone), and store the solution in a brown bottle.

The dithizone solution is checked photometrically before use. The absorbance of the solution (diluted 1 : 1 with Chloroform GR) should be 0.81 in a photometer or 1.0 in a spectrophotometer at 605 nm.

Potassium sodium tartrate solution: Dissolve 20 g Potassium sodium tartrate GR in 80 ml double-distilled water.

Solution I: Dissolve 20 g Sodium chloride cryst. GR and 10 ml Hydrazinium hydroxide about 24% N_2H_5OH with 70 ml 1 mol/l Hydrochloric acid in double-distilled water, and make up to 100 ml.

Solution II: Dissolve 20 g Potassium hydrogen carbonate GR, 5 g Potassium cyanide GR and 5 g Potassium sodium tartrate GR in 20 ml ammonia solution min. 25% (0.91) GR and a little double-distilled water, and make up to 100 ml with double-distilled water.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
9969	Lead standard solution Titrisol® 1.000 g ± 0.002 g Pb ($Pb(NO_3)_2$ in water)	1 amp.
7398	Lead(II) nitrate GR	1 kg
2442	Chloroform GR (for determinations with dithizone)	1 l, 2½ l
3092	Dithizone (1,5-diphenylthiocarbazone) GR	5 g, 25 g
4600	Hydrazinium hydroxide about 24% N_2H_5OH	1 l
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
4854	Potassium hydrogen carbonate GR	500 g
8087	Potassium sodium tartrate GR	500 g, 1 kg, 5 kg
6404	Sodium chloride cryst. GR	500 g, 1 kg, 5 kg
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
456	Nitric acid min. 65% (about 1.40) tested by the dithizone method GR	1 l, 2½ l
316	Nitric acid min. 25% (about 1.125) GR	1 l, 2½ l
9057	Hydrochloric acid 1 mol/l	1 l, 5 l
9970	Hydrochloric acid 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

2. Titrimetrically for higher concentrations

Suitable for determination of lead ions in concentrations greater than 10 mg/l Pb^{2+}.

Interferences and pre-treatment

Lead sulfide contained in the water sample is brought into solution with nitric acid. Lead sulfate and lead phosphate are dissolved in ammonium acetate solution.

In the presence of barium ions the lead ions are precipitated as lead sulfide with hydrogen sulfide. The precipitate is filtered off, and dissolved in nitric acid.

Procedure

Acidify 1000 ml of the water sample with 1 ml nitric acid, and evaporate to dryness on a water bath. Moisten the residue with 10 ml deionised water, 2 ml ammonium acetate solution and 3 ml acetic acid, and treat the solution with 2 ml potassium chromate solution. After about 90 min filter off the precipitate, and wash with deionised water until the filtrate is free from chromate ions. Dissolve the precipitate in 10 ml hydrochloric acid. Add 50 ml deionised water and 0.5 g potassium iodide, and after 10 min titrate against 0.01 mol/l sodium thiosulfate until colourless, using zinc iodide-starch solution as indicator.

Calculation

1 ml 0.01 mol/l sodium thiosulfate ≙ 0.691 mg Pb^{2+}
1 mmol lead ions ≙ 207.2 mg Pb^{2+}
mg/l Pb^{2+} = a × 0.691
a = ml of 0.01 mol/l sodium thiosulfate consumed

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Ammonium acetate solution: Dissolve 20 g Ammonium acetate GR in 80 ml deionised water.

Potassium chromate solution: Dissolve 10 g Potassium chromate GR in 90 ml deionised water.

Sodium thiosulfate solution 0.01 mol/l: Make 100 ml 0.1 mol/l Sodium thiosulfate solution up to 1000 ml with boiled and cooled deionised water as required. Add 0.2 g Sodium carbonate 10-hydrate cryst. GR to increase the stability.

Reagents

Cat. No.		Packages
1116	Ammonium acetate GR	500 g, 1 kg, 5 kg
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
4952	Potassium chromate GR	250 g, 1 kg
5043	Potassium iodide neutral GR	250 g, 1 kg, 2½ kg
6391	Sodium carbonate 10-hydrate cryst. GR	1 kg, 5 kg

9950	Sodium thiosulfate solution 0.1 mol/l Titrisol® concentrated solution *for preparation of 1 litre of 0.1 N solution*	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	1 l
454	Nitric acid min. 65% (about 1.40) GR	1 l, 2½ l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
823 310	Hydrogen sulfide	0.44 l
7996	Sulfidogen® (sulfur-paraffin) for generation of hydrogen sulfide	500 g
5445	Zinc iodide-starch solution GR	500 ml

Magnesium

Qualitative analysis

Treat 10 ml of the water sample with 0.2 ml titan yellow solution and 0.4 ml 4 mol/l sodium hydroxide. Depending on the magnesium ion concentration, an intense red colour or correspondingly coloured precipitate is produced. This colour can serve as a sensitive reaction for qualitative detection (1:500 000). Interfering elements which must be removed are: tin, aluminium, arsenic, bismuth and manganese. Barium, strontium and calcium permit detection even in 1000-fold excess. The reaction is also applicable after appropriate masking in the presence of beryllium, zinc, cadmium and not too high excesses of nickel and cobalt.

Reagent preparations

Sodium hydroxide 4 mol/l: Dissolve 16 g Sodium hydroxide pellets GR in deionised water to make 100 ml.

Titan yellow solution: Dissolve 0.1 g Titan yellow GR in deionised water to make 100 ml.

Reagents

Cat. No.		Packages
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
1307	Titan yellow (C.I. No. 19540, S. No. 280) GR (reagent for magnesium)	50 g

Rapid determination possible with Aquamerck® Reagent Kit
see Appendix

Quantitative analysis

Titrimetrically by means of Titriplex®III solution and indicator buffer tablets

Interferences and pre-treatment

Alkaline earths present are co-titrated. For the determination of magnesium in the presence of calcium ions see under "Calcium".

Iron and magnesium ions to a total of about 5 mg/l and aluminium ions to about 10 mg/l may be masked by triethanolamine.

The separation of aluminium-calcium-magnesium and zinc-magnesium is described in the Merck booklet "Complexometric Assay Methods with Titriplex".

Phosphates are removed before the determination with an anion exchanger.

Procedure

Approximately neutralise 100 ml of the water sample, or a smaller volume made up to 100 ml with deionised water, which should not contain more than 50 mg magnesium ions, with sodium hydroxide solution in the case of acid reaction. Add one indicator buffer tablet and, after the tablet has dissolved, 1 ml ammonia solution. Titrate with 0.1 mol/l Titriplex III solution until the colour changes from red to green. In the case of very small amounts of magnesium, the titration can also be carried out with 0.001 mol/l Titriplex III solution.

Calculation

1 ml 0.1 mol/l Titriplex III solution = 2.431 mg Mg^{2+} = 4.035 mg MgO

$$\text{mg/l } Mg^{2+} = \frac{a \times 2.431 \times 1000}{b}$$

a = ml of 0.1 mol/l Titriplex III solution consumed
b = ml of test water used
1 mmol magnesium ions ≙ 24.305 mg Mg^{2+}
1 meq magnesium ions ≙ 12.16 mg Mg^{2-}

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparation

Sodium hydroxide solution: Dissolve 10 g Sodium hydroxide pellets GR in 90 ml deionised water.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
8430	Indicator buffer tablets for determination of water hardness with Titriplex® solutions	500 tabl., 1000 tabl.
5240	Ion exchanger Merck Lewatit® MP 7080 GR 0.1–0.25 mm (60–150 mesh ASTM) weak-base anion exchanger macroporous OH^- form (® = trade mark of Bayer AG)	100 ml, 500 ml
4766	Ion exchanger II (weak-base anion exchanger) (LAB)	100 g, 500 g
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding gratuated in 0.5 pH units	1 pack
8431	Titriplex® III solution 0.1 mol/l metal (pM) indicator	1 l
9992	Titriplex® III solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 M solution	1 amp.

Manganese

Qualitative analysis

Boil 50 ml of the water sample with 5 ml nitric acid and a spatula-tip of lead(IV) oxide for 5–10 min. After the lead oxide has settled manganese is detected by a violet colouration of the supernatant liquid. The reaction fails in the presence of larger amounts of hydrochloric acid or chlorine compounds. Lower limit of detection: about 0.005 mg manganese.

Reagents

Cat. No.		Packages
7407	Lead(IV) oxide GR.	100 g, 250 g, 1 kg
454	Nitric acid min. 65% (about 1.40) GR	1 l 2½ l

Rapid determination possible with Merckoquant® Test Strips and with Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative analysis

1. Photometrically by means of formaldoxime

Suitable for determination of the total manganese in concentrations between 0.04 and 5 mg/l Mn (reported as manganese(II) ions).

Interferences and pre-treatment

Calcium and magnesium ions in concentrations greater than about 450 mg/l result in values which are too high. In such cases the water sample is correspondingly diluted with deionised water.

Phosphate ions above 10 mg/l only result in too low values in the presence of calcium ions; otherwise they do not interfere.

Substances causing turbidity must be centrifuged off after formation of the colour complex and before photometry.

In the case of coloured waters, Method 2 is to be used.

Procedure

Treat 50 ml of the test water successively with 5 ml formaldoxime solution, 5 ml ammonium iron(II) sulfate solution, 5 ml ammonia solution and – after about 5 min – 5 ml Titriplex III solution and 5 ml hydroxylammonium chloride solution, shaking the mixture on each addition. After 60 min, measure at 480 nm against a blank treated in the same manner.

The reference curve is prepared from dilution solutions of Manganese standard solution Titrisol treated in the same manner as the water sample.

Reporting of results

The values are rounded off to 0.01 mg/l for less than 1 mg/l, and to 0.05 mg/l for 1 mg/l or higher (reported as manganese(II) ions).

Reagent preparations

Ammonia solution: Mix 750 ml Ammonia solution min. 25% (0.91) GR with 250 ml deionised water.

Ammonium iron(II) sulfate solution: Dissolve 140 mg Ammonium iron(II) sulfate GR with 1 ml Sulfuric acid 95–97% (about 1.84) in deionised water, and make up to 1000 ml.

Formaldoxime solution: Dissolve 40 g Hydroxylammonium chloride GR and 8 g Paraformaldehyde Erg. B. 6 in deionised water to make 1000 ml.

Hydroxylammonium chloride solution: Dissolve 100 g Hydroxylammonium chloride GR in deionised water to make 1000 ml.

Manganese standard solution: Make the contents of one ampoule of Manganese standard solution Titrisol up to 1000 ml with deionised water. 1 ml ≙ 1 mg Mn as manganese(II) ions.

The dilutions necessary for plotting of the reference curve are freshly prepared from this solution as required.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
3793	Ammonium iron(II) sulfate (max. 0.002% Mn) GR	500 g
4616	Hydroxylammonium chloride GR	100 g, 250 g, 1 kg
9988	Manganese standard solution Titrisol® 1.000 g ± 0.002 g Mn ($MnCl_2$ in water)	1 amp.
4005	Paraformaldehyde Erg. B. 6	1 kg, 5 kg
8431	Titriplex® III solution 0.1 mol/l metal (pM) indicator	1 l
9992	Titriplex® solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 M solution	1 amp.
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

2. Photometrically by means of ammonium peroxodisulfate

Suitable for determination of the total manganese in concentrations between 0.1 and 4 mg/l Mn (reported as manganese(II) ions).

Interferences and pre-treatment

Chloride ions interfere; up to a concentration of 300 mg/l they are bound by addition of mercury nitrate solution (see under Procedure).

Organic substances – equivalent to a $KMnO_4$-consumption up to 60 mg/l – are decomposed by boiling with nitric acid (see Procedure).

If the content of chloride ions is greater than 300 mg/l and that of the organic substances above an equivalent $KMnO_4$-consumption of 60 mg/l, the 100 ml of water sample is evaporated with 5 ml ammonium peroxodisulfate, treated with about 3 ml sulfuric acid, and fumed. The residue is taken up with 5 ml nitric acid and 100 ml of boiled deionised water acidified with nitric acid.

Iron ions in concentrations greater than 5 mg/l are rendered inactive with 1 ml phosphoric acid before the oxidation with ammonium peroxodisulfate.

The chloride ion concentration is to be determined titrimetrically before the determination.

Procedure

Acidify 100 ml of the water sample, pre-treated as necessary, with 5 ml nitric acid, and treat with excess mercury nitrate solution in an amount equivalent to the chloride ion concentration + 2 ml. Heat to boiling, add 5 ml ammonium peroxodisulfate solution, and boil for 5 min. In the presence of manganese ions a pink to reddish-violet colour is produced depending on the concentration. Cool the solution immediately, and make up to 100 ml with boiled deionised water acidified with nitric acid. Measure at 530 nm against a blank of boiled deionised water acidified with nitric acid. If the test water is coloured, fill the comparison cell from a part of the available liquid which has been treated with oxalic acid until the reddish-violet colour disappears.

The reference curve is prepared from comparison solutions made up of varying dilutions of 0.01 mol/l potassium permanganate solution.

Reporting of results

The values are rounded off to 0.1 mg/l (reported as manganese(II) ions).

Reagent preparations

Ammonium peroxodisulfate solution: Dissolve 20 g Ammonium peroxodisulfate GR in 80 ml deionised water.

Potassium permanganate 0.002 mol/l: Dilute 100 ml 0.02 mol/l Potassium permanganate adjusted against oxalate to 1000 ml with boiled deionised water acidified with nitric acid, as required. 1 ml ≙ 1.099 mg as manganese ions.

The dilutions necessary for plotting of the reference curve are freshly prepared as required from this solution with boiled deionised water acidified with nitric acid. The titre of the 0.002 mol/l potassium permanganate must be checked against 0.005 mol/l oxalic acid before use.

Potassium permanganate 0.002 mol/l: Make the contents of one ampoule of 0.002 mol/l Potassium permanganate solution Titrisol concentrated solution for preparation of 1 litre 0.01 N solution adjusted against oxalate up to 1000 ml with boiled deionised water as required.

Oxalic acid 0.005 mol/l: Dilute 100 ml 0.05 mol/l oxalic acid to 1000 ml with deionised water as required.

Oxalic acid 0.005 mol/l: Make the contents of one ampoule of 0.005 mol/l oxalic acid solution Titrisol concentrated solution for preparation of 1 litre of 0.01 N solution up to 1000 ml with deionised water as required.

Mercury(II) nitrate 0.01 mol/l: Dilute 200 ml 0.05 mol/l Mercury(II) nitrate solution to 1000 ml with deionised water.

Nitric acid (about 1.20): Mix 500 ml Nitric acid min. 65% (about 1.40) GR with 500 ml deionised water.

Reagents

Cat. No.		Packages
1201	Ammonium peroxodisulfate GR	500 g, 1 kg, 5 kg
9935	Potassium permanganate solution 0.02 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution adjusted against oxalate	1 amp.
9930	Potassium permanganate solution 0.002 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.01 N solution adjusted against oxalate	1 amp.
9122	Potassium permanganate solution 0.02 mol/l adjusted against oxalate	1 l
9965	Oxalic acid solution 0.005 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9932	Oxalic acid solution 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.01 N solution	1 amp.
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
9143	Mercury(II) nitrate solution 0.05 mol/l	1 l
454	Nitric acid min. 65% (about 1.40) GR	1 l, 2½ l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

Rapid photometric analysis possible with Spectroquant® Manganese
see Appendix

Mercury

Quantitative analysis

Photometrically with dithizone

Suitable for determination of mercury ions in concentrations between 0.01 and 2.0 mg/l Hg^{2+}.

Interferences and pre-treatment

Silver, gold, palladium and platinum ions interfere at all concentrations.

The interference of larger concentrations of copper (Cu:Hg $> 10^3$) is eliminated as described under Procedure.

For determination of the total mercury, organically bound mercury must be mineralised before the quantitative estimation, and the volatility of most mercury compounds must be borne in mind: Boil 100 ml of the water sample for 2 h under reflux with 10 ml sulfuric acid (about 1.84) and sufficient potassium permanganate solution to leave a slight violet colouration at the end of the oxidation process. After cooling, decolourise, or dissolve precipitated manganese oxide, with a slight excess of hydroxylammonium chloride solution, boil, and cool to room-temperature.

Since mercury ions have a great tendency to adsorption, all glass apparatus should be carefully rinsed with dilute nitric acid, and then deionised water, before use.

Procedure

Introduce 100 ml, or smaller volume made up to 100 ml with deionised water, of the original water sample acidified with 0.5 mol/l sulfuric acid to pH 0–1, or 100 ml of the sample pre-treated as necessary, into a separating funnel, and extract with two 10.0 ml portions of dithizone solution. The last extract must remain green; if not, a smaller volume of the water made up to 100 ml with deionised water should be used.

If the water sample contains larger amounts of copper ($Cu:Hg > 10^3$), extract fractionally in the separating funnel as often as is required for the pure violet colour of copper dithizonate to appear. Shake the combined organic extracts twice for 2 min in each case with 15 ml 0.5 mol/l sulfuric acid and 1 ml potassium permanganate solution. The mercury goes into the aqueous phase, which is decolourised with a few drops of hydroxylammonium chloride solution. Now extract the aqueous phase with two 10.0-ml portions of dithizone solution.

Wash the combined organic extracts (from the treatment described in paras. 1 and/or 2) free from dithizone with three 10-ml portions of dilute ammonia solution, and then desensitise by shaking vigorously with 10 ml dilute acetic acid. After separation of the phases, drain the organic phase through a filter paper into a 2-cm cell, cover the cell immediately, and measure at 485 nm against a blank treated in the same manner.

The reference curve is prepared from standard solutions of mercury(II) chloride or dilution solutions of Mercury standard solution Titrisol treated in the same manner as the water sample.

Calculation

Any dilution of the water sample to 100 ml starting volume is to be taken into account in the calculation.

Reporting of results

The values are rounded off to 0.01 mg/l.
1 meq mercury(II) ions ≙ 100.30 mg Hg^{2+}.
1 mmol mercury(II) ions ≙ 200.59 mg Hg^{2+}.

Reagent preparations

Ammonia solution, dilute: Dilute 5 ml Ammonia solution min. 25% (0.91) GR to 1000 ml with deionised water.

Dithizone solution: Dissolve 0.02 g Dithizone GR by shaking for a longish period in 100 ml Carbon tetrachloride GR (for determinations with dithizone), and then extract with four 50-ml portions of dilute ammonia solution.

Filter the combined aqueous extracts through a plaited filter, add 100 ml Carbon tetrachloride GR and 1 ml Hydrochloric acid min. 25% (about 1.125), and shake immediately. Wash the green organic phase with three 50-ml portions of deionised water, and filter again. The solution is stable for about 4 weeks.

For the analysis a dilute solution of dithizone is employed which should be freshly prepared before use in each case: Make 10 ml of the dithizone stock solution up to 200 ml with Carbon tetrachloride GR.

Acetic acid, dilute: Dilute 15 ml Acetic acid glacial min. 96% (about 1.06) GR to 100 ml with deionised water.

Hydroxylammonium chloride solution: Dissolve 20 g Hydroxylammonium chloride GR in deionised water to make 100 ml.

Potassium permanganate solution: Saturated solution at room-temperature (about 6 g Potassium permanganate GR in 100 ml deionised water).

Mercury standard solution: Dissolve 1.354 g Mercury(II) chloride GR in 0.5 mol/l Sulfuric acid to make 1000 ml. 1 ml ≙ 1 mg Hg^{2+}.

For preparation of the reference curve fresh dilutions of this solution are made with 0.5 mol/l Sulfuric acid as required.

The Mercury standard solution Titrisol can also be used in a similar manner.

Nitric acid, dilute: Mix 100 ml Nitric acid min. 65% (about 1.40) tested by the dithizone method GR with 300 ml deionised water.

Reagents

Cat. No.		Packages
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
3092	Dithizone (1,5-diphenylthiocarbazone) GR	5 g, 25 g, 100 g
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
4619	Hydroxylammonium chloride (max. 0.000001% Hg) GR	250 g
5084	Potassium permanganate (max. 0.000005% Hg) GR	1 kg
4419	Mercury(II) chloride GR	50 g, 250 g, 1 kg
9916	Mercury standard solution Titrisol® 1.000 g ± 0.002 g Hg [$Hg(NO_3)_2$ in dil. nitric acid]	1 amp.
456	Nitric acid min. 65% (about 1.40) GR	1 l, 2½ l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
732	Sulfuric acid 95–97% (about 1.84) (max. 0.0000005% Hg) GR	2½ l
9072	Sulfuric acid 0.5 mol/l	1 l, 5 l
9981	Sulfuric acid 0.5 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9540	Special indicator strips pH 0–2.5 non-bleeding graduated in 0.5 pH units	1 pack
2208	Carbon tetrachloride GR (for determinations with dithizone)	1 l, 2½ l

Nitrate

Qualitative analysis

Treat 2 ml of the test water dropwise with 5 ml sulfuric acid and then with a little solid brucine (not more than 50 mg). In the presence of nitrate ions the solution at first develops a pale pink to cherry red colour depending on concentration which on standing becomes yellow to yellowish-brown. Lower limit of detection: about 1 mg/l NO_3^-.

Reagents

Cat. No.		Packages
1952	Brucine (dihydrate) GR	10 g, 50 g
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

Rapid determination possible with Merckoquant® Test Strips
see Appendix

Quantitative analysis

If the determination is not to take place within three hours of sampling, preserve the water sample with 1 ml of saturated mercury(II) chloride solution per 1000 ml. In this form the water may be kept for about two weeks for determination of the nitrate.

1. Photometrically by means of sodium salicylate

Suitable for determination of nitrate ions in concentrations between 0.1 and 20 mg/l NO_3^-.

Interferences and pre-treatment

Colloidal organic substances and colorants, and heavy metal ions, interfere in the determination; they may be eliminated by adding 5 ml aluminium sulfate solution to

100 ml of the water sample, and then sodium carbonate-sodium hydroxide solution until the reaction is alkaline. The resulting precipitate is filtered off.

Nitrite ions in concentrations greater than 2 mg/l are eliminated by evaporating the 20 ml water sample used in the determination on a water bath with addition of 0.05 g ammonium sulfate. The residue is further treated as described under Procedure.

In the case of a content of iron ions between 0.5 and 5 mg/l it is advisable to add double the amount (2 ml) of sodium salicylate solution (see under Procedure).

Water with a chloride ion concentration greater than 200 mg/l is treated as described under Procedure 1.2.

Procedure

1.1. in the case of a chloride ion concentration < 200 mg/l

Evaporate 20 ml of the clear or filtered and, where necessary, pre-treated water sample to dryness in a porcelain dish on a water bath with 1 ml (or 2 ml) sodium salicylate solution. Depending on the nitrate ion concentration, it is advisable to use various volumes of the water sample simultaneously by making them up to 20 ml with deionised water. Dry the residue for two hours at 150° C in a drying chamber, and allow to cool in a desiccator. Then add 2 ml sulfuric acid. – If the residue is discoloured by this addition, the method is not applicable for determination of the nitrate. – After 10 min, add 15.0 ml deionised water and 15.0 ml potassium sodium tartrate-sodium hydroxide solution with a pipette. After a further 10 min, measure at about 420 nm against a blank of 20 ml deionised water treated in the same manner.

The reference curve is prepared from standard solutions of sodium nitrate treated in the same manner as the water sample.

1.2. in the case of a chloride ion concentration > 200 mg/l

Determine the chloride ion content of 20 ml of the water sample diluted to 100 ml with deionised water by the method described on page 45, and record the consumption in ml of 0.0282 mol/l silver nitrate.

Then treat the 20 ml of the water sample for nitrate determination dropwise with the same number of ml of 0.0125 mol/l silver sulfate as were consumed in the chloride titration with 0.0282 mol/l silver nitrate. This corresponds to a slight excess for the quantitative precipitation of silver chloride. Clump the silver chloride precipitated by vigorous shaking, and filter off. Wash the residue on the filter with deionised water, and evaporate the clear filtrate to dryness on a water bath with 1 ml (or 2 ml) sodium salicylate solution. Then proceed as described under 1.1.

Note: Since the reagent Silver sulfate GR (Cat. No. 1509) cannot be guaranteed to be free from nitrate, a blank should always be prepared:

Adjust deionised water with a nitrate-free chloride salt to a chloride ion content corresponding to that of the water sample. Treat 20 ml of this solution with the same number of ml of 0.0125 mol/l silver sulfate, and treat further as described above.

Calculation

Any dilution of the water sample should be taken into account in evaluating the results.

Reporting of results

The values are rounded off to 0.1 mg/l for a nitrate ion content of less than 10 mg/l, and to 1 mg/l for 10 mg/l or higher.
1 mmol/nitrate ions ≙ 62.0 mg NO_3^-.

Reagent preparations

All solutions are prepared with nitrate-free deionised water.

Aluminium sulfate solution: Dissolve 120 g Aluminium sulfate cryst. pure DAB 7 in 1000 ml deionised water.

Potassium sodium tartrate-sodium hydroxide solution: Dissolve 60 g Potassium sodium tartrate GR and 400 g Sodium hydroxide pellets GR in deionised water to make 1000 ml. Store the solution in polyethylene bottles.

Sodium carbonate-sodium hydroxide solution: Dissolve 100 g Sodium carbonate 10-hydrate cryst. GR and 50 g Sodium hydroxide pellets GR in 300 ml deionised water.

Sodium salicylate solution: Dissolve 0.5 g Sodium salicylate cryst. GR in 100 ml deionised water. The solution should always be freshly prepared as required.

Nitrate standard solution: Dissolve 1.370 g Sodium nitrate GR with addition of 1 ml of saturated mercury(II) chloride solution in deionised water to make 1000 ml. 1 ml ≙ 1 mg NO_3^-.

The dilutions necessary for plotting of the reference curve are freshly prepared from this solution as required.

Mercury(II) chloride solution, saturated: Add 7–8 g Mercury(II) chloride GR to 100 ml deionised water.

Silver sulfate solution 0.0125 mol/l: Dissolve 3.898 g Silver sulfate GR in deionised water to make 1000 ml.

Reagents

Cat. No.		Packages
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
1102	Aluminium sulfate cryst. extra pure Ph. Eur.	1 kg, 5 kg
1217	Ammonium sulfate GR	1 kg, 5 kg
8087	Potassium sodium tartrate GR	500 g, 1 kg, 5 kg
6391	Sodium carbonate 10-hydrate cryst. GR	1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
6537	Sodium nitrate GR	500 g, 1 kg, 5 kg
6601	Sodium salicylate cryst. GR	250 g
4419	Mercury(II) chloride GR	50 g, 250 g, 1 kg
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
1509	Silver sulfate GR	25 g, 100 g

2. Photometrically or titrimetrically after reduction to ammonium ions and distillation

Suitable for determination of nitrate ions in concentrations greater than 0.1 mg/l by the photometric method and greater than 5 mg/l by the titrimetric method.

Interferences and pre-treatment

The interference from ammonium ions and substances which can form such ions is eliminated by evaporating the water sample together with sodium hydroxide solution before the reduction with Devarda's alloy (see under Procedure). Nitrite ions are co-reduced by Devarda's alloy. They must be determined separately, and taken into account in the evaluation.

2.1. Photometrically

Procedure

Introduce 500 ml of the water sample, or a smaller volume made up to 500 ml with ammonia-free deionised water according to the nitrate ion concentration, into a 1-l distillation flask with 30 ml sodium hydroxide solution, and evaporate to about

200 ml. After cooling of the solution, add 1 g Devarda's alloy, and immediately connect the flask with a vertical condenser whose outlet dips into a receiver containing 20–30 ml ammonia-free deionised water and 5 ml 0.1 mol/l hydrochloric acid. The reduction of the nitrate and nitrate ions proceeds at room-temperature, and is continued until the Devarda's alloy is consumed, i.e., has practically gone into solution. Then distill over about 100 ml, and make the volume up to 200 ml with ammonia-free deionised water. Take an aliquot portion (max. 50 ml) of this solution for photometric determination of the ammonium ions (see under Ammonium, page 7).

Calculation

The initial volume of water and the aliquot portion of the distillate used for determination are to be taken into account when evaluating the results.

The content of ammonium ions found is converted into nitrate ions according to the table on the next page.

The content on nitrite ions is to be subtracted from the result after conversion into nitrate ions by means of the table.

2.2. Titrimetric

Procedure

Introduce 500 ml of the water sample, or a smaller volume made up to 500 ml with ammonia-free deionised water according to the nitrate ion concentration, into a 1-l distillation flask with 30 ml sodium hydroxide solution, and evaporate to about 200 ml. After cooling of the solution, add 1 g Devarda's alloy, and immediately connect the flask with a vertical condenser whose outlet dips into a receiver containing 50 ml boric acid solution. The reduction of the nitrate and nitrite ions proceeds at room-temperature, and is continued until the Devarda's alloy is consumed, i.e., has practically gone into solution. Then distill over about 100 ml. Add 3 drops of mixed indicator 5 to the distillate, and titrate with 0.025 mol/l sulfuric acid until the colour changes from violet to green. For colour comparison, make up a blank of 50 ml boric acid solution diluted to about the same volume as the distillate with ammonia-free deionised water, and titrate with 0.025 mol/l sulfuric acid against mixed indicator 5.

Calculation

1 ml 0.025 mol/l sulfuric acid ≙ 3.10 mg NO_3^-

$$\text{mg/l } NO_3^- = \frac{a \times 3.10 \times 1000}{b} - c$$

a = ml of 0.025 mol/l sulfuric acid consumed
b = ml of test water used
c = content of nitrite ions in the water sample, converted to mg/l NO_3^-.

Conversion factors

1 mg		mg N	mg N_2O_3	mg NO_2^-	mg N_2O_5	mg NO_3^-	mg NH_4^+
N	is equiv. to	1.00	2.71	3.28	3.85	4.43	1.29
N_2O_3	is equiv. to	0.37	1.00	1.21	1.42	1.63	0.47
NO_2^-	is equiv. to	0.30	0.83	1.00	1.17	1.35	0.39
N_2O_5	is equiv. to	0.26	0.70	0.85	1.00	1.15	0.33
NO_3^-	is equiv. to	0.23	0.61	0.74	0.87	1.00	0.29
NH_4^+	is equiv. to	0.78	2.11	2.56	3.00	3.44	1.00

Reporting of results

The values are rounded off to 0.1 mg/l for a nitrate ion content of less than 10 mg/l, and to 1 mg/l for 10 mg/l or higher.
1 mmol nitrate ions ≙ 62.0 mg NO_3^-

Reagent preparations

All the solutions are prepared with nitrate- and ammonia-free deionised water.

Boric acid solution: Dissolve 40 g Boric acid cryst. GR in 1000 ml deionised water.

Deionised water, ammonia-free: Treat 1000 ml deionised water with 1 ml Sulfuric acid 95–97% (about 1.84) GR, and distill.

Sodium hydroxide solution: Dissolve 300 g Sodium hydroxide pellets GR in 700 ml deionised water.

Sulfuric acid 0.025 mol/l: Make 500 ml 0.05 mol/l Sulfuric acid up to 1000 ml with deionised water.

Reagents

Cat. No.		Packages
165	Boric acid cryst. GR	500 g, 1 kg, 2½ kg
5341	Devarda's alloy powder GR	250 g, 1 kg
6130	Mixed indicator 5 for ammonia titrations	250 ml
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
9060	Hydrochloric acid 0.1 mol/l	1 l, 5 l
9973	Hydrochloric acid 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9074	Sulfuric acid 0.05 mol/l	1 l, 5 l
9984	Sulfuric acid 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

Nitrite

Qualitative analysis

Treat 100 ml of water sample with 1.5 ml indole solution and 2.5 ml sulfuric acid. In the absence of interfering substances (for their elimination see under Quantitative analysis) a red to reddish-violet colour is produced after 5–10 min reaction time depending on the nitrite ion concentration. Lower limit of detection: about 0.02 mg/l NO_2^-.

Reagent preparations

Charcoal activated nitrite-free: Mix 100 g Charcoal activated GR with 2000 ml deionised water and 40 ml sodium hydroxide solution, and boil for a short time. Filter, and wash the activated charcoal on the filter with hydrochloric acid and then with deionised water until the reaction is neutral and the washings free from chloride. Dry the filter residue at 100° C in a drying chamber.

Indole solution: Dissolve 0.2 g Indole GR in Ethanol absolute GR to make 250 ml. The solution is ready for use after storage in the dark for 8 days. If a yellowish-brown colour subsequently develops, it can be eliminated by addition of nitrite-free activated charcoal, and filtration.

Sulfuric acid (about 1.27): Carefully pour 100 ml Sulfuric acid 95–97% (about 1.84) GR into 300 ml deionised water.

Reagents

Cat. No.		Packages
972	Ethanol absolute GR	1 l, 2½ l
2186	Charcoal activated GR	250 g, 1 kg
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
4730	Indole GR	10 g, 100 g
5590	Sodium hydroxide solution min. 32% (1.35) GR (for determination of nitrogen)	2½ l
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l

Rapid determination possible with Merckoquant® Test Strips and with Aquamerck®, Aquaquant® and Microquant® Reagent Kits
see Appendix

Quantitative analysis

Photometrically by means of sulfanilic acid and 1-naphthylamine

Suitable for determination of nitrite ions in concentrations between 0.02 and 0.6 mg/l NO_2^-.

Interference and pre-treatment

If the determination is not to be carried out within three hours of sampling, preserve the water sample with 1 ml of saturated mercury(II) chloride solution per 1000 ml. In this form the water may be kept for about two weeks for determination of the nitrite.

Colloidal organic substances, humic acid and free chlorine interfere in the determination; they are eliminated by shaking the water sample with 1–2 g nitrite-free activated charcoal per 100 ml, and filtering after 5 min reaction time. Before the treatment with activated charcoal the water sample is adjusted to pH > 8.5, in order to avoid adsorption of the nitrite ions onto the activated charcoal.

The above-mentioned interfering substances, together with heavy metal ions, may also be removed by treating 100 ml of the water sample with 5 ml aluminium sulfate solution and then with sodium carbonate-sodium hydroxide solution until an alkaline reaction is given. The resulting precipitate is filtered off.

Procedure

Treat 50 ml of the water sample, pre-treated as necessary, or a smaller volume made up to 50 ml with deionised water according to the nitrite ion concentration, with 2 ml of a mixture of equal volumes of sulfanilic acid solution and 1-naphthylamine solution, mix well, and after 60 min reaction time, during which the solution is to be protected from direct sunlight, measure at about 530 nm against a blank of 50 ml deionised water treated in the same manner.

The reference curve is prepared from standard solutions of sodium nitrite treated in the same manner as the water sample.

Calculation

Any dilutions of the water sample are to be taken into account in evaluating the results.

Reporting of results

The values are rounded off to 0.01 mg/l for a nitrite ion content of less than 0.1 mg/l, to 0.05 mg/l for 0.1 to 1.0 mg/l, and to 0.1 mg/l for more than 1.0 mg/l.

Reagent preparations

Charcoal activated, nitrite-free: Mix 100 g Charcoal activated GR with 2000 ml deionised water and 40 ml sodium hydroxide solution, and boil for a short time. Filter and wash the activated charcoal on the filter with hydrochloric acid and then with deionised water until the reaction is neutral and the washings free from chloride. Dry the filter residue at 100° C in a drying chamber.

Aluminium sulfate solution: Dissolve 120 g Aluminium sulfate extra cryst. pure Ph. Eur. in 1000 ml deionised water.

1-Naphthylamine solution: Dissolve 0.1 g 1-Naphthylamine GR in 10 ml Acetic acid glacial min. 96% (about 1.06) and 40 ml deionised water, and dilute the solution to 250 ml with deionised water.

Sodium carbonate-sodium hydroxide solution: Dissolve 100 g Sodium carbonate 10-hydrate cryst. GR and 50 g Sodium hydroxide pellets GR in 300 ml deionised water.

Sodium hydroxide solution: Dissolve 32 g Sodium hydroxide pellets GR in deionised water to make 100 ml.

Nitrite standard solution: Dry Sodium nitrite cryst. GR in a vacuum desiccator. Dissolve 1.500 g in deionised water, add 1 ml saturated mercury(II) chloride solution, and make up to 1000 ml with deionised water. 1 ml $\triangleq$ 1 mg NO_2^-.

The nitrite ion content of the solution is established by titration with potassium permanganate, and the titre standardised accurately. On storage of the solution, the titre must be checked again before use.

The dilutions necessary for plotting of the reference curve are freshly prepared from this solution as required.

Mercury(II) chloride solution saturated: Add 7–8 g Mercury(II) chloride GR to 100 ml deionised water.

Sulfanilic acid solution: Heat 1 g Sulfanilic acid GR with 15 ml Acetic acid glacial min. 96% (about 1.06) and 15 ml deionised water, and dissolve by addition of 270 ml hot deionised water. The sulfanilic acid only dissolves slowly, so that it may be necessary to heat again. Store the solution in a brown bottle in a cool place.

Reagents

Cat. No.		Packages
2186	Charcoal activated GR	250 g, 1 kg
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
1102	Aluminium sulfate cryst. extra pure Ph. Eur.	1 kg, 5 kg
62	Acetit acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
6245	1-Naphthylamine GR	100 g, 500 g
6391	Sodium carbonate 10-hydrate cryst. GR	1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
6549	Sodium nitrite cryst. GR	500 g
5590	Sodium hydroxide solution min. 32% (1.35) GR (for determination of nitrogen)	2½ l
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
4419	Mercury(II) chloride GR	50 g, 250 g, 1 kg
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
686	Sulfanilic acid GR	100 g, 250 g

Rapid photometric analysis possible with Spectroquant® Nitrite
see Appendix

Nitrogen

Determination of total nitrogen

In the presence of reduced and oxidised nitrogen

The term total nitrogen signifies the total amount of nitrogen present in the bound form:

$$N_{total} = N_{NH_4^+} + N_{org.} + N_{NO_2^-} + N_{NO_3^-}$$

"reduced nitrogen" "oxidised nitrogen"

Preservation

Samples taken should be analysed without delay. Where this is not possible, the sample must be preserved. Short-term storage (up to a few hours) in a refrigerator or under cooling with ice is permissible; for storage in the longer term the sample is preserved immediately by chemical means: Measure the initial volume into a Kjeldahl flask, and treat with 5 ml sulfuric acid-hydrogen peroxide solution (see under Procedure), thus oxidising the chemically labile nitrite to stable nitrate and reducing the pH of the water sample to a value so low that microbial reactions are no longer possible.

Procedure

The initial volume of the water sample and the method of determination depend on the content of total nitrogen to be expected:

mg/l N	ml initial volume	Method of determination
< 2	50	photometric
2–10	10	
10–140	50	titrimetric
140–300	20	
>300	10	

Depending on the nitrogen content to be expected, treat 10–50 ml of the water sample in a long-necked 100-ml Kjeldahl flask with 5 ml sulfuric acid-hydrogen peroxide solution, bring slowly to the boil within 20–30 min, and keep gently boiling for about 15 min. After cooling (in a water bath if necessary), add 10 ml sulfuric acid, and cool again to at least room-temperature. Then add 600–800 mg iron (always in the same amount within ±5% for all determinations), and allow to stand with occasional swirling for 30 min or swirl in a shaking machine.

Dissolve the iron remaining after the reduction completely by gradually heating, and add 2.5–3.0 g selenium reaction mixture to the solution.

Then heat the sample at even and gentle boiling until the salt residue is a pure yolk-yellow, the liquid water-white and the air space above the liquid only filled with a thin white mist. As a precaution, heat the mixture for a further 30 min. – If compounds difficult to decompose are present in the sample, e.g., compounds containing the pyridine ring or the quinoline ring system in the molecule such as nicotinic acid or quinoline derivatives, heating can be required for a longer period – up to 6 hours or more – although the liquid in the flask has long been colourless.

After cooling, carefully dilute the decomposed sample with about 25 ml ammonium-free deionised water, and transfer quantitatively to the distillation vessel of an ammonia distillation apparatus. Add 50 ml sodium hydroxide solution (1.35), wash down with a little ammonium-free deionised water, and begin the distillation with the outlet of the condenser dipping into the absorption agent required for the particular method of determination:

1. Photometric determination

100-ml volumetric flask containing about 15 ml ammonium-free deionised water and 5 ml 0.02 mol/l hydrochloric acid.

Distill over to below the mark, lower the volumetric flask, wash the outlet tube from outside, and remove the receiver from the apparatus shortly before the mark is reached. Then make up to the mark with ammonium-free deionised water, and carry out a photometric determination of the nitrogen content of an aliquot portion of the distillate as ammonium ions (see under "Ammonium", page 7).

For every determination prepare a blank of ammonium-free deionised water treated in the same manner.

Calculation and Reporting of results

See under "Ammonium".

The initial volumes and the aliquot portion of the distillate used for the determination are to be taken into account in the determination.

2. Titrimetric determination

300-ml conical flask containing 25.0 ml 0.02 mol/l acid and 2–3 drops mixed indicator 5 for ammonia titrations.

If the indicator changes colour during the distillation, and this is noticed in good time, add a further 25.0 ml 0.02 mol/l hydrochloric acid with a pipette.

After about 150 ml has been distilled over, lower the flask, wash the outlet tube from outside, and in the meantime continue distilling for about 1 min. Then titrate the sample with 0.02 mol/l sodium hydroxide until the colour changes from reddish-violet to greyish-green.

For every determination prepare a blank treated in the same manner.

Calculation

$$\text{mg/l N} = \frac{(a-b) \times 280.1}{c}$$

a = ml of 0.02 mol/l sodium hydroxide consumed in the case of the blank
b = ml of 0.02 mol/l sodium hydroxide consumed in the case of the water sample
a and b must apply to the same starting volume of 0.02 mol/l hydrochloric acid
c = ml of test water used

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

All solutions are prepared with ammonium-free deionised water.

Deionised water, ammonium-free: Treat deionised water with 1 ml Sulfuric acid 95–97% (about 1.84) GR per 1000 ml, and distill.

Sulfuric acid-hydrogen peroxide solution: Carefully pour 200 ml Sulfuric acid 95–97% (about 1.84) GR into 275 ml deionised water. After cooling, add 25 ml Perhydrol 30% H_2O_2 GR. The solution is stable for a few weeks when protected from direct sunlight and heat.

Reagents

Cat. No.		Packages
3819	Iron reduced GR	100 g, 500 g
6130	Mixed indicator 5 for ammonia titrations	250 ml
5590	Sodium hydroxide solution min. 32% (1.35) GR (for determination of nitrogen)	2½ l
9142	Sodium hydroxide solution 0.02 mol/l	500 ml
7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
9054	Hydrochloric acid 0.02 mol/l	4 l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
8030	Selenium reaction mixture GR (for determination of nitrogen acc. to Wieninger)	250 g, 1 kg, 5 kg

Calculation of the organically bound nitrogen

The term organically bound nitrogen signifies the nitrogen contained in organic compounds which cannot be detected analytically as nitrate, nitrite or ammonia nitrogen.

After determination of the total nitrogen and the nitrate, nitrite and ammonia nitrogen, the organically bound nitrogen can be calculated by the following formula:

mg/l org. N = $a-(b \times 0.23 + c \times 0.30 + d \times 0.78)$
a = mg/l total N
b = mg/l NO_3
c = mg/l NO_2
d = mg/l $NH_4^{\cdot}$

Nitrogen

Conversion factors

1 mg		mg N	mg NH_3	mg NH_4^+	mg N_2O_3	mg NO_2	mg N_2O_5	mg NO_3^-
N	is equiv. to	1.00	1.21	1.29	2.71	3.28	3.85	4.43
NH_3	is equiv. to	0.82	1.00	1.06	2.24	2.70	3.17	3.64
NH_4^+	is equiv. to	0.78	0.94	1.00	2.11	2.55	2.99	3.44
N_2O_3	is equiv. to	0.37	0.45	0.47	1.00	1.21	1.42	1.63
NO_2^-	is equiv. to	0.30	0.37	0.39	0.83	1.00	1.17	1.35
N_2O_5	is equiv. to	0.26	0.32	0.33	0.70	0.85	1.00	1.15
NO_3^-	is equiv. to	0.23	0.27	0.29	0.61	0.74	0.87	1.00

Oils and fats

The determination of oils and fats can occasionally also result in concomitant determination of other compounds extractable with petroleum benzine and having a *boiling* point above about *200° C*, in *total* concentrations greater than *1* ml/l.

Interferences and pre-treatment

The above-mentioned organic compounds include, for example, waxes, emulsifiers, and detergents. Low-boiling point hydrocarbons (petrol) are not co-determined.

Salts of fatty acids (soaps) are not co-determined. Should these be co-determined in the form of fatty acids, the sample is brought to a pH value below 2 with sulfuric acid before the extraction, the sample not being acidified until after the first extraction.

Formation of emulsions during extraction can be avoided by acidifying to pH 1 or by addition of sodium chloride.

All the glass apparatus must be carefully cleaned before sampling or determination, washed out with petroleum benzine, and dried. Particular care should be taken that the ground glass joints are free from grease.

Sampling

It is most expedient to use a glass-stoppered glass bottle, and fill the latter up to a certain ring mark (e.g., 500 ml).

Procedure

1. In the case of waters with little contamination

Transfer the entire contents of the sampling bottle to a 1000-ml separating funnel, rinse the bottle out with one or two 10-ml portions of petroleum benzine, and add the solvent to the water sample. Then make the volume of the petroleum benzine up to 25 ml, and shake the sample thoroughly for about 2 min. After separation of the layers, run the aqueous phase into a second 1000-ml separating funnel, and the organic phase into a 100-ml separating funnel. Repeat the extraction with two 15-ml portions of petroleum benzine. Rinse the separating funnels used in the extraction with about 5–10 ml petroleum benzine, and combine the solvent with the extract in the 100-ml separating funnel.

If the extract contains finely dispersed substances, the latter can be sedimented by centrifugation (15 min at about 3000 rpm).

Use a vacuum rotary evaporator for further treatment of the extract.

Filter the extract – centrifuged as necessary – into a weighed 100-ml evaporating flask through a soft filter paper containing an insert of fat-free cottonwool and previously washed with petroleum benzine. Then fix the flask to the steam-conduction tube of the vacuum rotary evaporator with an ST-clip, and suspend it in a water bath with temperature regulated at 20 ± 1°C by means of a thermostat. Evacuate the flask at a moderate rpm with the aid of a water-jet pump until the pressure has fallen to about 50 torr and the residual volume of the extract is about 0.5 ml. Shortly prior to this, start up an oil-sealed vacuum pump, and when the residual volume of the extract has reached about 0.5 ml, connect this pump with the apparatus by turning a three-way stopcock. Then evaporate for about 5 min at about 25 torr (if possible, at about 2 torr). Relieve the vacuum and decrease the rotation, carefully remove the flask, wipe the outside, dry for 60 min in a desiccator over silica gel, and weigh.

2. In the case of heavily contaminated waters or sludges containing water

Evaporate 500 ml or less of the sample of water or sludge to dryness in a porcelain dish with 30 g sea sand on a water bath. Transfer the residue quantitatively to a Soxhlet extraction thimble, and place the latter in a Soxhlet apparatus. Rinse out the dish with petroleum benzine. Extract with petroleum benzine for 3–4 h. Then connect the extraction flask to a vacuum rotary evaporator and evaporate the solvent to about 10 ml.

Proceed as described under 1. with stepwise – where necessary – centrifugation, filter into a weighed evaporator flask, and treat further in the vacuum rotary evaporator.

Calculation

$$\text{Total oil and fat or petroleum benzine extract in mg/l} = \frac{a \times 1000}{b}$$

a = weight in mg of extraction residue
b = ml of water or sludge sample used

Reporting of results

The values are rounded off to 1 mg/l.

Reagent preparation

Sulfuric acid 1 mol/l: Make the contents of one ampoule of 0.5 mol/l Sulfuric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution up to 500 ml with deionised water.

Reagents

Cat. No.		Packages
9531	Acilit® indicator strips pH 0–6.0 non-bleeding graduated in 0.5 pH units	1 pack
1925	Silica gel with moisture indicator (blue gel) (LAB)	1 kg, 5 kg
6404	Sodium chloride cryst. GR	500 g, 1 kg, 5 kg
1775	Petroleum benzine GR boiling range 50–60°C	1 l, 5 l
9981	Sulfuric acid 0.5 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
7712	Sea sand purified by acid calcined GR	500 g, 1 kg, 5 kg

Oxygen

Determination of dissolved oxygen

Qualitative analysis

Fill an oxygen-determination bottle (clear-glass bottle of 110–130 ml capacity with bevelled glass stopper and capacity exactly known to 0.1 ml) to overflowing with the test water, avoiding the inclusion of air bubbles. Add 0.5 ml each of manganese(II) chloride solution and sodium hydroxide solution containing potassium iodide, close the bottle without inclusion of air bubbles, and shake well. Depending on the oxygen content, a white (oxygen-free) to dark-brown (oxygen-rich) colour is produced.

Rapid determination possible with Aquamerck® Reagent Kits

see Appendix

Quantitative analysis

1. Volumetrically according to Winkler

Suitable for determination of dissolved oxygen in concentrations greater than 0.5 mg/l.

Interferences and pre-treatment

Most oxidising and reducing substances, e.g., dissolved organic substances (potassium permanganate-consuming capacity greater than 60 mg/l), nitrite ions, higher-valency manganese compounds, active chlorine, sulfide and sulfite ions, iron(II) and iron(III) ions interfere.

The influence of the dissolved organic substances can be excluded by conversion of the manganese hydroxides into oxygen-sensitive carbonates by subsequent addition of 4 ml ammonium hydrogen carbonate solution.

Nitrite ions are decomposed by addition of sodium azide (contained in the sodium hydroxide solution reagent).

Iron(II) ions are determined, and taken into account in calculation of the oxygen content. 1 mg/l Fe^{2+} is equivalent to a consumption of 0.14 mg/l O_2.

Iron(III) ions are rendered inactive during the determination by addition of phosphoric acid.

The interference of all oxidising and reducing substances can be excluded by application of the Ohle iodine-difference method (see under 2.).

Procedure

Fill an oxygen-determination bottle (clear-glass bottle of 110–130 ml capacity with bevelled glass stopper and capacity exactly known to 0.1 ml) to overflowing with the test water, avoiding the inclusion of air bubbles. Add 0.5 ml each of manganese(II) chloride solution and sodium hydroxide solution containing potassium iodide by means of oxygen pipettes, close the bottle without inclusion of air bubbles, and shake vigorously. After the precipitate has settled, carefully decant or suction off the clear supernatant liquid, and dissolve in 2 ml phosphoric acid. Allow the closed bottle to stand for 10 min in the dark.

Titrate the iodine liberated against 0.01 mol/l (or 0.0125 mol/l) sodium thiosulfate until colourless, using zinc iodide-starch solution as indicator. Do not add the zinc iodide-starch solution until towards the end of the titration, i.e., when the solution has become pale yellow.

Calculation

1 ml 0.01 mol/l sodium thiosulfate $\triangleq$ 0.08 mg O_2

$$\text{mg/l } O_2 = \frac{a \times 0.08 \times 1000}{V - b}$$

a = ml of 0.01 mol/l sodium thiosulfate consumed
V = volume of the oxygen-determination bottle in ml
b = ml of water (1.0 ml) displaced by the reagents added

Where 0.0125 mol/l sodium thiosulfate is used:
1 ml 0.0125 mol/l sodium thiosulfate $\triangleq$ 0.1 mg O_2

$$\text{mg/l } O_2 = \frac{a \times 100}{V - b}$$

Reporting of results

The values are rounded off to 1.0 mg O_2/l.

Reagent preparations

Ammonium hydrogen carbonate solution: Dissolve 70 g Ammonium hydrogen carbonate in 185 ml deionised water.

Manganese(II) chloride solution mol/l: Dissolve 800 g Manganese(II) chloride GR in 1000 ml deionised water.

Sodium thiosulfate 0.01 mol/l: Make 100 ml 0.1 mol/l Sodium thiosulfate up to 1000 ml with boiled and cooled deionised water as required. Add 0.2 g Sodium carbonate 10-hydrate cryst. GR to increase the stability.

Sodium thiosulfate 0.0125 mol/l: Make 125 ml 0.1 mol/l Sodium thiosulfate up to 1000 ml with boiled and cooled deionised water as required. Add 0.2 g Sodium carbonate 10-hydrate cryst. GR to increase stability.

Sodium hydroxide solution, containing potassium iodide: Dissolve 360 g Sodium hydroxide pellets GR, 200 g Potassium iodide neutral GR and 5 g Sodium azide in deionised water to make 1000 ml (Caution, protective goggles!). Filter the solution through asbestos or glass wool.

Reagents

Cat. No.		Packages
1131	Ammonium hydrogen carbonate powder	5 kg
1560	Asbestos for Gooch crucibles (LAB)	50 g, 250 g, 1 kg
4086	Glass wool (LAB)	500 g
5043	Potassium iodide neutral GR	100 g, 250 g, 1 kg
5927	Manganese(II) chloride GR	100 g, 1 kg
822 335	Sodium azide for synthesis	100 g, 250 g
6391	Sodium carbonate 10-hydrate cryst. GR	1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
9950	Sodium thiosulfate solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	500 ml, 1 l
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
5445	Zinc iodide-starch solution GR	500 ml

2. Volumetrically with the Ohle iodine-difference method

Suitable for determination of dissolved oxygen in concentrations greater than 0.5 mg/l O_2 in the presence of iodine-consuming and oxidising substances of organic and inorganic nature.

Procedure

Fill two oxygen-determination bottles (for description see under 1.) designated H (main sample) and P (parallel sample) to overflowing with the test water, avoiding the inclusion of air bubbles. Place 1.00 ml iodine solution (= 4 mg I_2) at the bottom of each bottle by means of a pipette or injection syringe (capacity 5 or 10 ml, 0.05 ml divisions). If the amount of iodine is not adequate, it can be increased. Close the bottles without inclusion of air bubbles, shake well, and if they are not to be further treated immediately store in the dark in water or damp cloths.

To bottle H add 1.0 ml manganese(II) chloride-magnesium chloride solution and 1.0 ml sodium hydroxide solution containing potassium iodide in that order, and to bottle P 1.0 ml magnesium chloride solution and 1.0 ml sodium hydroxide solution containing potassium iodide. Close again without inclusion of air bubbles, and shake well. After the precipitate has settled, carefully decant or suction off the clear supernatant solution. Dissolve the precipitates each in 3.0 ml hydrochloric acid (about 1.125) and titrate the solutions with 0.01 mol/l or 0.0125 mol/l sodium thiosulfate until colourless, using zinc iodide-starch solution as indicator towards the end of the titration.

Calculation

1 ml 0.01 mol/l sodium thiosulfate $\triangleq$ 0.08 mg O_2
1 ml 0.0125 mol/l sodium thiosulfate $\triangleq$ 0.1 mg O_2

$$\text{mg/l } O_2 = \left[\frac{(B-P)\times 1000}{V_P - 3} + \frac{(H-B)\times 1000}{V_H - 3}\right] \times 0.08$$

B = blank value in ml of the iodine solution titrated against 0.01 mol/l sodium thiosulfate
P = ml of 0.01 mol/l sodium thiosulfate consumed with the parallel sample
H = ml of 0.01 mol/l sodium thiosulfate consumed with the main sample
V_P = contents of the parallel sample bottle in ml
V_H = contents of the main sample bottle in ml

Where 0.0125 mol/l sodium thiosulfate is used, multiplication in the formula is by 0.01 instead of by 0.08.

The formula applies for addition of 1.00 ml iodine solution to the bottles. If more iodine has been necessary, this must be taken into account in the calculation. If the water sample contains oxidising substances which liberate iodine, then P is greater than B.

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Iodine solution:

a) **Iodine stock solution:** Dissolve 5 g Iodine resublimed GR and 100 g Potassium iodide neutral GR in 80 ml boiled deionised water (total volume about 114 ml). 1 ml of this contains about 44 mg iodine and about 880 mg potassium iodide.

b) **Sodium chloride solution, saturated:** Dissolve 35 g Sodium chloride cryst. GR in 100 ml boiled deionised water, and filter the solution.

Mix 10.0 ml Solution a and 100 ml Solution b. 1 ml of this solution contains about 4.0 mg iodine and 80 mg potassium iodide.

Magnesium chloride solution: Dissolve 150 g Magnesium chloride GR in 200 ml boiled deionised water, and filter the solution.

Manganese(II) chloride-magnesium chloride solution: Dissolve 100 g Manganese(II) chloride GR and 50 g Magnesium chloride GR in 200 ml boiled deionised water, and filter the solution.

Sodium thiosulfate 0.01 mol/l: For preparation see under 1.

Sodium thiosulfate 0.0125 mol/l: For preparation see under 1.

Sodium hydroxide solution, containing potassium iodide: Dissolve 200 g Sodium hydroxide pellets GR, 100 g Potassium iodide GR and 3.0 g Sodium azide in 400 ml boiled deionised water. 1 ml of this solution contains about 6 mg sodium azide and 250 mg potassium iodide.

Reagents

Cat.No.		Packages
4761	Iodine resublimed GR	100 g, 500 g, 1 kg
5043	Potassium iodide neutral GR	100 g, 250 g, 1 kg, 2½ kg

5833	Magnesium chloride GR	250 g, 1 kg, 5 kg
5927	Manganese(II) chloride GR	100 g, 1 kg
822 335	Sodium azide for synthesis	100 g, 250 g
6404	Sodium chloride cryst. GR	500 g, 1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
9950	Sodium thiosulfate solution 0.1 mol/l Titrisol concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	500 ml, 1 l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
5445	Zinc iodide-starch solution GR	250 ml

3. Volumetrically with the difference method in the case of lower concentrations (Deutsche Einheitsverfahren, J 8)

Suitable for determination of dissolved oxygen in concentrations between 5 and 200 $\mu g/l$ O_2 in boiler and boiler feed waters.

Sampling

Sampling must be carried out with great care, so that no air can penetrate into the water sample. The latter is taken at the condenser, which is enclosed by a sheet-metal casing filled to above the stuffing box of the valve with glycerin or a viscous oil.

Two oxygen-determination bottles (clear-glass bottles of 550–650 ml capacity with bevelled glass stopper and volume exactly known to 0.1 ml) are used, the one being designation "ox" and the other "red". For sampling the bottle "ox" is placed in a tin bucket whose rim stands about 5 cm above the upper edge of the neck of the bottle. It is weighted with a lead ring to hold it steady. The water is led to the bottom of the bottle through a glass tube connected to the condenser by means of a rubber tube. The water is allowed to overflow the bottle for 10 min. The glass tube is then carefully removed from the bottle without interrupting the flow of water. 1.5 ml each of manganese(II) chloride solution and potassium hydroxide solution containing potassium iodide are added in that order through the water layer standing above the mouth of the bottle by means of oxygen pipettes or injection syringes. After insertion of the stopper under water, the bottle is taken out of the bucket, shaken well, and replaced in the bucket for about 10 min to allow the precipitate to settle.

The bottel "red" can be filled to overflowing with water outside the bucket, and closed with the glass stopper.

Procedure

Add 5.5 ml sulfuric acid to the bottle "ox" a little below the water level, close again immediately, and shake well. Measure out 500 ml of the contents with a graduated cylinder, and transfer to a 1000-ml conical flask containing 20 ml sodium acetate solution. Successively add 1 g potassium iodide, and by means of a burette 10 ml 0.0005 mol/l iodine (or a larger volume if required) and 2 ml starch solution. Titrate the sample with a microburette against 0.00625 mol/l sodium thiosulfate until colourless.

Measure 500 ml from the bottle "red" with a graduated cylinder, and transfer to a conical flask containing 20 ml sodium acetate solution. Successively add 3.5 ml sulfuric acid, 1 g potassium iodide, and by means of a burette 10 ml 0.0005 mol/l iodine (or a larger volume if required) and 2 ml starch solution. Titrate with a microburette against 0.00625 mol/l sodium thiosulfate until colourless.

Calculation

1 ml 0.00625 mol/l sodium thiosulfate $\triangleq$ 50 μg O_2

$$\text{mg/l } O_2 = \frac{(a-b) \times 50 \times 1000}{500} = (a-b) \times 100$$

a = ml of 0.00625 mol/l sodium thiosulfate consumed with bottle "ox"
b = ml of 0.00625 mol/l sodium thiosulfate consumed with bottle "red"
1 mmol oxygen $\triangleq$ 16.00 mg O_2

Reporting of results

The values are rounded off to 1 μg/l.

Reagent preparations

Iodine 0.0005 mol/l: Make 10 ml 0.05 mol/l Iodine solution up to 1000 ml with deionised water. (Prepare the solution fresh as required.)

Potassium hydroxide, containing potassium iodide: Dissolve 700 g Potassium hydroxide pellets GR in 550 ml deionised water and 150 g Potassium iodide neutral GR in 150 ml deionised water. Add the potassium iodide solution to the cooled potassium hydroxide solution. The solution mixture should not exhibit any separation of iodine on acidification.

Manganese(II) chloride solution: Dissolve 800 g Manganese(II) chloride GR in 1000 ml deionised water.

Sodium acetate solution: Dissolve 450 g Sodium acetate cryst. GR indifferent to potassium permanganate in a little deionised water, and make up to 1000 ml.

Sodium thiosulfate 0.00625 mol/l: Make 62.5 ml 0.1 mol/l Sodium thiosulfate solution up to 1000 ml with deionised water.

Sulfuric acid (about 1.53): Carefully pour 100 ml Sulfuric acid 95–97% (about 1.84) GR into 100 ml deionised water.

Starch solution: Heat a mixture of 500 ml Glycerin redistilled (about 87%) GR and 500 ml deionised water to boiling. Stir 10 g Starch soluble GR into 20–30 ml deionised water, add to the heated mixture, and boil together for a further 3 min. – The solution is stable for long periods.

Reagents

Cat. No.		Packages
4094	Glycerin redistilled (about 87%) GR	500 ml, 1 l, 5 l
9910	Iodine solution 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9099	Iodine solution 0.05 mol/l	1 l
5033	Potassium hydroxide pellets GR	500 g, 1 kg, 5 kg
5043	Potassium iodide neutral GR	100 g, 250 g, 1 kg, 2½ kg
5927	Manganese(II) chloride GR	100 g, 1 kg
6267	Sodium acetate cryst. GR	500 g, 1 kg, 5 kg
9950	Sodium thiosulfate solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	1 l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
1252	Starch soluble GR	100 g, 250 g, 1 kg

Oxygen saturation, oxygen saturation index, oxygen deficit

1. Oxygen saturation:

The concentration of oxygen in a water which is in equilibrium with the atmosphere in dependence on the temperature and on the air pressure obtaining at the surface of the water. The values are ascertained from the table on page 154.

Table for determination of the oxygen saturation in dependence on the temperature at a total pressure of the water-vapour-saturated atmosphere of 760 torr according to Truesdale, Downing and Lowden

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t°C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					mg O_2/l					
0	14.16	14.12	14.08	14.04	14.00	13.97	13.93	13.89	13.85	13.81
1	13.77	13.74	13.70	13.66	13.63	13.59	13.55	13.51	13.48	13.44
2	13.40	13.37	13.33	13.30	13.26	13.22	13.19	13.15	13.12	13.08
3	13.05	13.01	12.98	12.94	12.91	12.87	12.84	12.81	12.77	12.74
4	12.70	12.67	12.64	12.60	12.57	12.54	12.51	12.47	12.44	12.41
5	12.37	12.34	12.31	12.28	12.25	12.22	12.18	12.15	12.12	12.09
6	12.06	12.03	12.00	11.97	11.94	11.91	11.88	11.85	11.82	11.79
7	11.76	11.73	11.70	11.67	11.64	11.61	11.58	11.55	11.52	11.50
8	11.47	11.44	11.41	11.38	11.36	11.33	11.30	11.27	11.25	11.22
9	11.19	11.16	11.14	11.11	11.08	11.06	11.03	11.00	10.98	10.95
10	10.92	10.90	10.87	10.85	10.82	10.80	10.77	10.75	10.72	10.70
11	10.67	10.65	10.62	10.60	10.57	10.55	10.53	10.50	10.48	10.45
12	10.43	10.40	10.38	10.36	10.34	10.31	10.29	10.27	10.24	10.22
13	10.20	10.17	10.15	10.13	10.11	10.09	10.06	10.04	10.02	10.00
14	9.98	9.95	9.93	9.91	9.89	9.87	9.85	9.83	9.81	9.78
15	9.76	9.74	9.72	9.70	9.68	9.66	9.64	9.62	9.60	9.58
16	9.56	9.54	9.52	9.50	9.48	9.46	9.45	9.43	9.41	9.39
17	9.37	9.35	9.33	9.31	9.30	9.28	9.26	9.24	9.22	9.20
18	9.18	9.17	9.15	9.13	9.12	9.10	9.08	9.06	9.04	9.03
19	9.01	8.99	8.98	8.96	8.94	8.93	8.91	8.89	8.88	8.86
20	8.84	8.83	8.81	8.79	8.78	8.76	8.75	8.73	8.71	8.70
21	8.68	8.67	8.65	8.64	8.62	8.61	8.59	8.58	8.56	8.55
22	8.53	8.52	8.50	8.49	8.47	8.46	8.44	8.43	8.41	8.40
23	8.38	8.37	8.36	8.34	8.33	8.32	8.30	8.29	8.27	8.26
24	8.25	8.23	8.22	8.21	8.19	8.18	8.17	8.15	8.14	8.13
25	8.11	8.10	8.09	8.07	8.06	8.05	8.04	8.02	8.01	8.00
26	7.99	7.97	7.96	7.95	7.94	7.92	7.91	7.90	7.89	7.88
27	7.86	7.85	7.84	7.83	7.82	7.81	7.79	7.78	7.77	7.76
28	7.75	7.74	7.72	7.71	7.70	7.69	7.68	7.67	7.66	7.65
29	7.64	7.62	7.61	7.60	7.59	7.58	7.57	7.56	7.55	7.54
30	7.53	7.52	7.51	7.50	7.48	7.47	7.46	7.45	7.44	7.43
31	7.42	7.41	7.40	7.39	7.38	7.37	7.36	7.35	7.34	7.33
32	7.32	7.31	7.30	7.29	7.28	7.27	7.26	7.25	7.24	7.23
33	7.22	7.21	7.20	7.20	7.19	7.18	7.17	7.16	7.15	7.14
34	7.13	7.12	7.11	7.10	7.09	7.08	7.07	7.06	7.05	7.05
35	7.04	7.03	7.02	7.01	7.00	6.99	6.98	6.97	6.96	6.95
36	6.94	6.94	6.93	6.92	6.91	6.90	6.89	6.88	6.87	9.86
37	6.86	6.85	6.84	6.83	6.82	6.81	6.80	6.79	6.78	6.77
38	6.76	6.76	6.75	6.74	6.73	6.72	6.71	6.70	6.70	6.69
39	6.68	6.67	6.66	6.65	6.64	6.63	6.63	6.62	6.61	6.60
40	6.59	6.58	6.57	6.56	6.56	6.55	6.54	6.53	6.52	6.51

2. Oxygen saturation index:

The oxygen content of a water expressed as a percentage of the oxygen saturation value. It is reported in whole percents.

3. Oxygen deficit:

The difference between the oxygen content of a water determined and the oxygen saturation value in mg/l O_2 corresponding to the water temperature at the time of sampling.

Oxygen consumption

The oxygen consumption is ascertained from the difference between the oxygen content of a water immediately after sampling and after a duration of consumption of 48 hours. It is a measure of the 48-hour oxygen requirement of the microorganisms contained in the water for decomposition of the degradable organic constituents.

The method is suitable for water samples in which the oxygen concentration after the duration of the consumption is still greater than 2 mg/l O_2.

Procedure

Fill two calibrated oxygen-determination bottles of about 300 ml capacity to overflowing with test water, avoiding the inclusion of air bubbles. Determine the oxygen in one bottle immediately (see Determination of dissolved oxygen, page 147). Close the second bottle without addition of chemicals, avoiding inclusion of air bubbles, and store in the dark (preferably in an incubator) at 20°C for 48 hours. Then determine the oxygen in this bottle also.

Calculation

Calculate the difference between the oxygen concentration in the first and in the second bottle in mg/l O_2.

Reporting of results

The values are rounded off to 0.1 mg/l.

The **chemical** oxygen consumption is ascertained from the difference between the oxygen content of a water immediately after sampling and after a duration of consumption of 2 hours. The procedure and calculation are otherwise as given above. The chemical oxygen consumption is a measure of the oxygen requirement of a water for chemical oxidation of constituents without the intervention of microorganisms.

pH value

The hydrogen ion concentration (pH) of aqueous solutions signifies the hydronium ion concentration $C_{H_3O^+}$.

1. Colorimetrically

1.1 With Aquamerck® Reagent Kits for the determination of pH in water (see Part III). The reagent kits are suitable for the measurement of weak and unbuffered, colourless waters. The colour scales are graduated in 0.5 pH units in the range 4.5–9.0.

1.2 With Universal indicator solution (pH 4–10),
Indicator solution (pH 0–5) and
Indicator solution (pH 9–13).

Add 3 drops Universal indicator solution to about 5 ml water. The scale provided is graduated in 0.5 pH units within the pH range 4–10. Intermediate values can be estimated.

Strongly acid waters can be measured in the same manner with Indicator solution (pH 0–5) and strongly alkaline waters with Indicator solution (pH 9–13).

1.3 With non-bleeding pH indicator strips and indicator papers

A greater accuracy of reading can be attained with non-bleeding pH indicator strips, particularly in the case of usually heavily buffered waste waters. The Special indicator strips and papers are accurate up to 0.2 pH units.

In the case of turbid or coloured waters the colour of the pH indicator paper is only evaluated on that part of the strip which is not immersed in the water but is moistened by suction of the water. The non-bleeding indicator strips should be briefly rinsed after immersion.

The high accuracy of measurement of the non-bleeding indicator strips is only fully utilised when the strips are left in the water sample until no further change in colour is produced. In the case of weakly buffered waters it can be necessary to wait several minutes. Since the indicator colours do not bleed, this does not create any difficulty.

Reagents

Cat. No.		Packages
9177	Indicator solution including colour scale (pH 0–5.0)	100 ml
9176	Indicator solution including colour scale (pH 9–13.0)	100 ml
9175	Universal indicator solution including colour scale pH 0–14.0	100 ml, 1 l
	Aquamerck® pH Reagent Kits, see Part III	
	Special indicator papers graduated in 0.2–0.3 pH units:	
9555	pH 3.8–5.4 including colour scale	1 pack
9556	pH 5.4–7.0 including colour scale	1 pack
9557	pH 6.4–8.0 including colour scale	1 pack
9558	pH 8.2–10.0 including colour scale	1 pack
	Special indicator strips non-bleeding graduated in whole pH units:	
9535	Universal indicator strips pH 0–14	1 pack
	graduated in 0.5 pH units:	
9531	Acilit® indicator strips pH 0–6	1 pack
9533	Neutralit® indicator strips pH 5–10	1 pack
9532	Alkalit® indicator strips pH 7.5–14	1 pack
	Special indicator strips non-bleeding graduated in 0.2–0.3 pH units:	
9540	pH 0 – 2.5	1 pack
9541	pH 2.5– 4.5	1 pack
9542	pH 4.0– 7.0	1 pack
9543	pH 6.5–10.0	1 pack
9545	pH 11.0–13.0	1 pack

2. Electrometrically

It is beyond the scope of this book to do more than make a reference to the possibility of highly accurate pH measurements by means of pH meters or valve voltmeter. Such electrometric measurements only have to be undertaken when the accuracy of the indicator methods, which decreases with buffering of the water, would be insufficient.

Phenols

Qualitative analysis

If a marked odour of phenols is produced on shaking of the water sample in a stoppered bottle, then at least 1 mg/l is present.

If the water sample is treated with dilute chlorine water and shaken well, far lower concentrations of phenols are detectable by the iodoform-like odour produced.

Reagent preparation

Chlorine water, dilute: Pass chlorine into deionised water until 1 ml is about equivalent to 1 mg Cl_2.

Reagents

Cat. No.		Packages
823 235	Chlorine (laboratory gas).	0.44 l
823 236	Chlorine (laboratory gas).	5.0 l

Quantitative analysis

1. Photometrically by means of 4-nitroaniline

Suitable for determination of phenols in concentrations between 0.05 and 5.0 mg/l.

Organic substances with phenol groups and amines are co-determined.

Polyvalent phenols and phenol homologues are determined to different extents, and on photometric evaluation can therefore yield higher or lower results referred to the equivalent amount of phenol (C_6H_5OH).

Pre-treatment

If the water sample is tested immediately after sampling, preservation may be omitted. Otherwise a glass-stoppered bottle should be charged with sodium hydroxide solution (1 ml per 100 ml water), filled to overflowing with the water sample, the stopper inserted, and the bottle well shaken. The water should then give a strong alkaline reaction. In this form it is stable for some days.

1.1. Total phenols

Procedure

If the test water is alkaline, neutralise with sulfuric acid. Filter through a plaited filter. The water employed in the analysis must be clear and colourless, otherwise Method 2 should be used for the determination of total phenols.

Allow 1.5 ml sodium nitrite solution to act on 5 ml 4-nitroaniline solution for 2 min, thus decolorising the solution. Then add 50 ml of the water sample, or a smaller volume made up to 50 ml with deionised water depending on the phenol concentration (taking into account eventual addition of sulfuric acid for neutralisation of a pre-treated sample) and 5 ml of a 20% sodium carbonate solution, and shake well. After exactly 10 min reaction time, measure at 470 nm against a blank treated in the same manner.

The reference curve is prepared from standard solutions of phenol treated in the same manner as the test water.

1.2. Steam-distillable phenols

Interferences

The interference of sulfide ions is excluded by addition of copper(II) sulfate solution, and that of cyanide ions by addition of cobalt(II) sulfate ions on distillation.

Procedure

The distillation apparatus consists of a 500-ml distillation flask, bulb attachment, Liebig condenser (in each case with ground-glass connections) and a 250- or 500-ml receiver with marking.

Introduce 250 ml of the water sample into the distillation flask, add 1 ml each of

copper(II) sulfate and cobalt(II) solutions if necessary, and then treat with 10 ml phosphoric acid. Charge the receiver with deionised water and 10 ml of 0.5 mol/l sodium carbonate solution, and distill until about 20 ml remains in the flask.

If the expected phenol concentration is more than a few mg/l, the steam-distillable phenols are estimated by adding about 100 ml deionised water to the distillation residue in the flask, and distilling again until about 20 ml remains. In the case of very low phenol concentrations, this part of the procedure is dispensed with, in order to avoid unnecessary dilution of the distillate.

When distillation is complete, make the volume in the receiver up to 250 or 500 ml (on repeated distillation) with deionised water.

Treat 50 ml of distillate, or an aliquot portion thereof made up to 50 ml with deionised water, as described under 1.1, and measure in a photometer.

Calculation

In calculation of the total phenols any dilution of the water sample, and of the steam-distillable phenols the starting volume of water, the volume of the made-up distillate and the aliquot portion thereof used in the determination are to be taken into account.

Reporting of results

The values are rounded off to 0.005 mg/l, designated as "total phenols" or "steam-distillable phenols".

Reagent preparations

Cobalt(II) sulfate solution: Dissolve 10 g Cobalt(II) sulfate GR in 100 ml deionised water.

Copper(II) sulfate solution: Dissolve 10 g Copper(II) sulfate 5-hydrate GR in 100 ml deionised water.

Sodium carbonate about 0.5 mol/l: Dissolve 53 g Sodium carbonate anhydrous GR in deionised water, and make up to 1000 ml.

Sodium carbonate solution (20%): Dissolve 20 g Sodium carbonate anhydrous GR in deionised water to make 100 ml.

Sodium hydroxide solution: Dissolve 40 g Sodium hydroxide pellets GR in deionised water, and make up to 100 ml.

Sodium nitrite solution: Dissolve 1 g Sodium nitrite cryst. GR in deionised water to make 100 ml. Prepare the solution fresh as required.

4-Nitroaniline solution: Dissolve 0.1 g 4-Nitroaniline for determination of phenol in 10 ml Acetic acid glacial min. 96% (about 1.06) GR, and make up to 100 ml with deionised water.

Phenol standard solution: Dissolve 1.000 g Phenol stabilised GR in deionised water to make 1000 ml. The solution must be clear and colourless. 1 ml ≙ 1 mg phenol.

The dilutions of this solution required for plotting of the reference curve are prepared fresh as required.

Reagents

Cat. No.		Packages
9532	Alkalit® indicator strips pH 7.5–14 non-bleeding graduated in 0.5 pH units	1 pack
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2½ l
2556	Cobalt(II) sulfate GR	100 g, 250 g
2790	Copper(II) sulfate 5-hydrate GR	250 g, 1 kg, 5 kg
6392	Sodium carbonate anhydrous GR	500 g, 1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
6549	Sodium nitrite cryst. GR	500 g
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
6760	4-Nitroaniline for determination of phenol	50 g
207	Phenol stabilised GR	250 g, 1 kg
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
716	Sulfuric acid 25% GR	1 l

2. Photometrically by means of 1-phenyl-2,3-dimethyl-4-amino-5-pyrazolone

Suitable for determination of phenols in concentrations between 0.02 and 1.0 mg/l. The following are determined:

Phenol, ortho- and meta-compounds of phenol, and depending on pH value, p-compounds of phenol with carboxyl, halogen, methoxyl or sulfonic acid groups.

The following are not determined:

p-Compounds of phenol with alkyl, aryl, nitro, benzoyl, nitroso or aldehyde groups.

Interferences and pre-treatment

In order to suppress biochemical and chemical oxidations, the water sample is brought to a pH below 4 immediately after sampling by addition of phosphoric acid, and briefly stirred or aerated when sulfur compounds are present. 1 g Copper(II) sulfate 5-hydrate is then added per litre of water, mixed, and the bottle closed. If stored in a cool place the water sample is stable for some days in this form.

If the determination of phenol is carried out immediately after sampling the treatment described may be dispensed with.

Oxidising substances, i.e., those which reveal themselves by liberation of iodine after acidification in the presence of potassium iodide, are eliminated by addition of an excess of iron(II) sulfate or sodium meta-arsenite immediately after sampling.

Procedure

2.1. Total phenols

Treat 250 ml of the water sample, or a smaller volume made up to 250 ml with deionised water depending on the phenol concentration, in a 500-ml separating funnel with 40 ml buffer solution, 2 ml 1-phenyl-2,3-dimethyl-4-amino-5-pyrazolone solution, and after 2 min with 5 ml potassium hexacyanoferrate(III) solution. Shake the mixture after each addition. Shake the resulting colour complex with 30 ml chloroform evenly for 2 min. After 15–30 min run the organic phase through a small, dry filter paper into a cell, and immediately measure at 470 nm against a blank treated in the same manner.

The reference curve is prepared from standard of phenol treated in the same manner as the water sample.

2.2 Steam-distillable phenols

The distillation apparatus consists of a 500-ml distillation flask, bulb attachment, Liebig condenser (in each case with ground-glass connections), and 250-ml graduated cylinder as receiver.

Introduce 250 ml of the water sample into the distillation flask, adjust the pH value to below 4 with phosphoric acid using methyl orange as indicator, and treat with 5 ml copper(II) sulfate solution.

If the water has already been preserved on sampling, these additions can be dispensed with.

Distill over 200 ml, add 50 ml of phenol-free deionised water, and continue the distillation until the graduated cylinder contains 250 ml distillate.

The volume of the distillate should always be the same as the starting volume of the water sample.

Proceed further with 250 ml distillate, or an aliquot portion thereof made up to 250 ml with phenol-free deionised water, as described unter 2.1.

Calculation

In calculation of the total phenols any dilution of the water sample, and of the steam-distillable phenols any dilution of the distillate for the determination, should be taken into account.

Reporting of results

The values are rounded off to 0.005 mg/l, designated as "total phenols" or "steam-distillable phenols".

Reagent preparations

All solutions to be prepared with phenol-free, chlorine-free deionised water.

Potassium hexacyanoferrate(III) solution: Dissolve 8.0 g Potassium hexacyanoferrate(III) GR in deionised water to make 100 ml. The solution is stable for about 1 week.

Copper(II) sulfate solution: Dissolve 100 g Copper(II) sulfate 5-hydrate GR in deionised water to make 1000 ml.

Phenol standard solution: Dissolve 1.000 g Phenol stabilised GR in deionised water to make 1000 ml. The solution must be clear and colourless. 1 ml $\triangleq$ 1 mg phenol.

The dilutions of this solution necessary for plotting of the reference curve are prepared fresh as required.

1-Phenyl-2,3-dimethyl-4-amino-5-pyrazolone solution: Dissolve 2.0 g 1-Phenyl-2,3-dimethyl-4-amino-5-pyrazolone GR in deionised water to make 100 ml. This solution should be prepared fresh daily before use.

Phosphoric acid: Mix 10 ml ortho-Phosphoric acid min. 85% (about 1.71) GR with 85 ml deionised water.

Buffer solution: Make 350 ml Ammonia solution min. 25% (0.91) GR and 54 g Ammonium chloride up to 1000 ml with deionised water.

Note: Waste waters treated with pure phenol solutions are preserved by Method 1 alkaline and by Method 2 acid. The waters are stable for up to 6 days when stored in a cool place, i.e., the phenol values measured in the various water samples remain constant from the 1st to the 6th day.

Reagents

Cat.No.		Packages
9531	Acilit® indicator strips pH 0.6.0 non-bleeding graduated in 0.5 pH units	1 pack
5432	Ammonia solution min. 25% (0.91) GR	1 l 2½ l, 5 l
1145	Ammonium chloride GR	500 g, 1 kg, 5 kg
2442	Chloroform GR (for determinations with dithizone)	1 l, 2½ l
3965	Iron(II) sulfate GR	500 g, 1 kg, 5 kg
4973	Potassium hexacyanoferrate(III) GR	250 g, 1 kg
5043	Potassium iodide neutral GR	100 g, 250 g, 1 kg, 2½ kg
2790	Copper(II) sulfate 5-hydrate GR	250 g, 1 kg, 5 kg
1323	Methyl orange solution 0.1% indicator	250 ml, 1 l
6287	Sodium meta-arsenite GR	250 g, 1 kg
207	Phenol stabilised GR	250 g, 1 kg
7293	1-Phenyl-2,3-dimethyl-4-amino-5-pyrazolone GR	10 g, 100 g
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l

Phosphate

Qualitative analysis

A spatula-tip of sodium chloride, a few drops of ammonium molybdate solution acidified with sulfuric acid, and a strip of tinfoil are added to 10 ml of water sample in that order. In the presence of phosphate ions a blue colour is produced.

Reagent preparations

Ammonium molybdate solution, acidified with sulfuric acid: Dissolve 10 g Ammonium heptamolybdate GR in 100 ml deionised water. Carefully mix 100 ml of the solution with 100 ml sulfuric acid (about 1.22).

Sulfuric acid (about 1.22): Carefully add 25 ml Sulfuric acid 95–97% (about 1.84) GR to 100 ml deionised water.

Reagents

Cat. No.		Packages
1182	Ammonium heptamolybdate (ammonium molybdate) GR	250 g, 1 kg, 5 kg
6404	Sodium chloride cryst. GR	500 g, 1 kg, 5 kg
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
7826	Tinfoil 0.04 mm GR	1 pack

Rapid determination possible with Aquamerck®, Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative analysis

Suitable for determination of ortho-phosphate ions in concentrations from 0.1 to about 12 mg/l PO_4^{3-}.

Interferences and pre-treatment

Iron ions interfere in concentrations greater than 1 mg/l; the water sample is correspondingly diluted where necessary with deionised water.

Turbid water must be filtered until clear over a membrane filter before the determination.

All the glass apparatus used should be thoroughly cleaned before the determination, care being taken not to employ any phosphate-containing detergent.

Procedure

1. Determination of the ortho-phosphate ion concentration

Treat 50 ml of the water sample, or a smaller volume made up to 50 ml with deionised water depending on the ortho-phosphate ion concentration, with 10 ml vanadate-molybdate reagent, and after 15 min reaction time measure at 405 nm against a blank treated in the same manner.

The reference curve is prepared from standard solutions of di-sodium hydrogen phosphate treated in the same manner as the test water.

2. Determination of the total phosphate concentration

Acidify 50 ml or less of the water sample, depending on the phosphate ion content, with a little nitric acid (about 1.40) in an appropriately sized test-tube, and evaporate to dryness on a water bath. Heat the residue carefully with 4 g potassium nitrate-sodium carbonate mixture to a pale yellow, clear melt, with continuous rotation of the test-tube. The end-point is indicated by foaming of the melt. After cooling of the melt, dissolve in 15 ml nitric acid (about 1.14), and make up to 50 ml with deionised water.

Treat 50 ml deionised water in the same manner as a blank.

Proceed further with both solutions as described under 1.

Calculation

Any dilutions of the water sample should be taken into account in the calculation. The difference in the values from determinations 1. and 2. yields the content of polyphosphates in the water.

1 meq ortho-phosphate ions = 31.67 mg PO_4^{3-}
1 mmol ortho-phosphate ions = 94.97 mg PO_4^{3-}

Reporting of results

The values are rounded off to 0.1 mg/l. If the content is less than 0.1 mg/l, the results are reported as 0.0 mg/l.

Reagent preparations

Potassium nitrate-sodium carbonate mixture: Carefully mix 3 parts Potassium nitrate GR with 1 part Sodium carbonate anhydrous GR.

Phosphate standard solution: Dissolve 1.874 g di-Sodium hydrogen phosphate 2-hydrate GR in deionised water, and make up to 1000 ml. 1 ml $\triangleq$ 1 mg PO_4^{3-}.

The dilutions of this solution necessary for plotting of the reference curve are prepared fresh as required. Store in a cool place, and for not longer than 1 week.

Nitric acid (about 1.14): Add 42 ml Nitric acid min 65% (about 1.40) GR to 100 ml deionised water.

Reagents

Cat. No.		Packages
5063	Potassium nitrate GR	500 g, 1 kg, 5 kg
6392	Sodium carbonate anhydrous GR	500 g, 1 kg, 5 kg
6580	di-Sodium hydrogen phosphate 2-hydrate GR	500 g, 1 kg, 5 kg
454	Nitric acid min. 65 (about 1.40) GR	1 l, 2½
8498	Vanadate-molybdate reagent for determination of phosphate	500 ml

Rapid photometric analysis possible with Spectroquant® Phosphorus
see Appendix

Potassium permanganate-consuming capacity

The organic substances carbohydrates, phenols and sulfite waste liquors (from cellulose) are oxidised to a large extent by potassium permanganate, protein products to a minor extent, detergents and ballast substances of organic synthesis in the field of plastics (phthalic acid, benzoic acid, low fatty acids, alcohols, ketones) not at all.

Qualitative analysis

The test water is acidified in a test-tube with dilute sulfuric acid, heated, and treated with a few drops of 0.002 mol/l potassium permanganate. The solution is decolourised to a greater or lesser extent depending on the content of organic substances oxidisable by potassium permanganate in the water.

Reagent preparations

See under Quantitative analysis

Quantitative analysis

Suitable for determination of potassium permanganate-consuming capacity greater than 1 mg/l in all waters.

1. Titrimetrically at a chloride-ion content less than 300 mg/l Cl^-

Interferences and pre-treatment

Oxidisable inorganic constituents, particularly sulfide, nitrite and chloride ions, and free hydrogen sulfide interfere in the determination.

Sulfide and nitrite ions, and free hydrogen sulfide are removed by boiling 100 ml of the water sample with 5 ml sulfuric acid (see Procedure).

At more than 300 mg/l Cl^-, either the water sample is diluted or the determination carried out in alkaline solution as described under 2.

If the test water contains substances in coarse dispersion, and their $KMnO_4$-consuming capacity is to be co-determined, the sample is homogenised, preferably for about 3 min in a mixer.

If the $KMnO_4$-consuming capacity of the sedimentable substances is to be disregarded, the sample is clarified for 2 h in an *Imhoff* funnel and decanted before determination.

If the $KMnO_4$-consuming capacity of the substances dissolved in the water is to be determined, the latter is filtered through a soft, plaited filter, or preferably through a glass-fibre filter.

Procedure

Use 300-ml-narrow-necked conical flasks which have been boiled out before use with potassium permanganate solution (an approx. 10-fold dilution of the 0.002 mol/l solution) acidified with sulfuric acid. Keep exclusively for determination of the $KMnO_4$-consuming capacity, and store protected from dust. Do not rinse after use.

To 100 ml of the water sample – pre-treated as necessary – in a conical flask add 5 ml sulfuric acid, attach a bulb condenser, and heat rapidly to boiling. Treat the boiling solution with 15.0 ml 0.002 mol/l potassium permanganate, and keep gently and evenly boiling for exactly 10 min after attaching the bulb condenser. Then add 15.0 ml 0.005 mol/l oxalic acid with a pipette, and continue boiling until the mixture is decolourised. Back-titrate the hot solution with 0.002 mol/l potassium permanganate until a pink colour just is produced which persists for a short time. The consumption should be between 3 and 10 ml 0.002 mol/l potassium permanganate; if it is higher, repeat the determination with a smaller volume of test water made up to 100 ml with dilution water.

2. Titrimetrically at a chloride-ion content greater than 300 mg/l Cl^-

Interferences and pre-treatment

Oxidisable *inorganic* substances, particularly free hydrogen sulfide, sulfide, nitrite and iron(II) ions interfere in the determination. Their content is determined separately and taken into account in calculation of the results.

Otherwise the procedure is as under 1.

Procedure

The determination is carried out as given under 1. except that before boiling 0.5 ml sodium hydroxide solution is added instead of the 5 ml sulfuric acid, and 5 ml sulfuric acid after the addition with a pipette of the 15.0 ml 0.005 mol/l oxalic acid.

Calculation

1 ml 0.002 mol/l potassium permanganate ≙ 0.316 mg $KMnO_4$

$$\text{mg/l } KMnO_4 = \frac{[(15 + a) \times f - 15] \times 0.316 \times 1000}{b}$$

a = ml of 0.002 mol/l potassium permanganate consumed
f = factor of the 0.002 mol/l potassium permanganate

$$= \frac{15.0 \text{ ml}}{x \text{ ml comsumption for titre}}$$ (for determination of titre see Reagent preparations)

b = ml of test water used

In the case of Method 2 the following may have to be subtracted from the results:

for 1 mg/l Fe^{2+}	0.57 mg/l $KMnO_4$
for 1 mg/l NO_2^-	1.37 mg/l $KMnO_4$
for 1 mg/l H_2S	1.86 mg/l $KMnO_4$

Reporting of results

The results are rounded off to 0.1 mg/l for a potassium permanganate consumption of less than 10 mg/l, to 1 mg/l for 10 to 100 mg/l, to 10 mg/l for 100 to 1000 mg/l, and to 100 mg/l for higher than 1000 mg/l.

Reagent preparations

Potassium permanganate 0.002 mol/l: Make 100 ml 0.02 mol/l Potassium permanganate solution adjusted against oxalate up to 1000 ml with boiled deionised water as required, or make the contents of one ampoule of Potassium permanganate solution Titrisol concentrated solution for preparation of 1 litre of 0.01 N solution adjusted against oxalate up to 1000 ml with deionised water.

The titre of this solution must be re-determined daily before use: Titrate a sample to a slightly pink end-point in accordance with Method 1 or 2, treat with 15.0 ml 0.005 mol/l oxalic acid, and where necessary heat briefly until the solution is decolourised. Back-titrate with 0.002 mol/l potassium permanganate until the same pink colour is produced. The consumption should be between 14.5 and 15.5 ml 0.002 mol/l potassium permanganate. Substitute the number of ml consumed for x under the formula for f (see Calculation).

Oxalic acid 0.005 mol/l: Make 100 ml 0.05 mol/l oxalic acid solution up to 1000 ml with deionised water as required, or make the contents of one ampoule of 0.005 mol/l Oxalic acid solution Titrisol concentrated solution for preparation of 1 litre of 0.01 N solution up to 1000 ml with deionised water.

Sulfuric acid (about 1.27): Carefully mix 100 ml Sulfuric and 95–97% (about 1.84) GR with 300 ml deionised water. Treat the still hot solution with 0.002 mol/l potassium permanganate until a pink colour is just produced.

Dilution water: Acidify deionised water with sulfuric acid; boil, and treat the still hot water with 0.002 mol/l potassium permanganate until a pink colour is just produced.

Reagents

Cat.No.		Packages
9122	Potassium permanganate solution 0.02 mol/l adjusted against oxalate	1 l
9930	Potassium permanganate solution 0.002 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.01 N solution adjusted against oxalate	1 amp.
9935	Potassium permanganate solution 0.02 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution adjusted against oxalate	1 amp.
5590	Sodium hydroxide solution min. 32% (1.35) GR (for determination of nitrogen)	2½ l
9932	Oxalic acid solution 0.005 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.01 N solution	1 amp.
9965	Oxalic acid solution 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
731	Sulfuric acid 95–97 % (about 1.84) GR	1 l, 2½ l

Silicic acid (Silicate, Silicon)

Qualitative analysis

The test water is acidified in a test-tube with hydrochloric acid, and treated with a knife blade-tip of solid ammonium molybdate. In the presence of dissolved silicic acid or silicate ions a more or less intense yellow colour is produced on swirling (phosphates interfere).

Lower limit of detection: about 0.1 mg/l SiO_2

Reagents

Cat.No.		Packages
1182	Ammonium heptamolybdate (ammonium molybdate) GR	100 g, 250 g, 1 kg, 5 kg
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l

Rapid determination possible with Aquamerck®, Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative analysis

Suitable for determination of dissolved silicic acid and silicate ions in concentrations from 0.02 to 9.0 mg/l SiO_2.

Interferences and pre-treatment

Phosphate ions interfere; up to 20 mg/l P_2O_5 is masked during the determination by oxalic acid solution. If higher concentrations are present, the water sample is diluted with silicic acid-free, double-distilled water.

The simultaneous presence of aluminium and phosphate ions removes the masking effect of the oxalic acid again. In order to exclude the interference, an additional masking with 0.2 ml potassium cyanide solution per sample volume is recommended. Higher concentrations of reducing agents in the water are to be decomposed before the determination proper.

Procedure

Use plastic bottles for sampling, and plastic pipettes for pipetting.

Treat 50 ml of the water sample in a plastic conical flask with 2 ml ammonium molybdate solution, and swirl well. After exactly 5 min, add 2 ml oxalic acid solution, and swirl again. After exactly 1 min, mix with 2 ml Photo-Rex solution. After 10 min reaction time, measure at 820 nm against a blank treated in the same manner. The temperature of the solutions measured should be between 20 and 25° C.

Measuring range of the 0.5-cm cell max. to 9.0 mg/l SiO_2,
2-cm cell max. to 4.0 mg/l SiO_2,
5-cm cell max. to 0.5 mg/l SiO_2

The reference curves are prepared by means of dilution solutions of a silicon standard solution treated in the same manner as the test water.

Reporting of results

The values are rounded off to 0.001 mg/l for a silicic acid content of less than 0.1 mg/l, to 0.01 mg/l for 0.1 to 1.0 mg/l, and to 0.1 mg/l for more than 1.0 mg/l.

Reagent preparations

All the solutions are prepared in plastic vessels, and stored in plastic bottles.

Ammonium molybdate solution: Dissolve 5 g Ammonium heptamolybdate (ammonium molybdate) GR in a 100-ml volumetric flask with a little silicic acid-free, double-distilled water, treat with 5 ml Sulfuric acid 95–97% (about 1.84) GR, and make up to the mark with silicic acid-free, double-distilled water.

Potassium cyanide solution: Dissolve 10 g Potassium cyanide GR in silicic acid-free, double-distilled water to make 100 ml.

Oxalic acid solution: Dissolve 5 g Oxalic acid GR in silicic acid-free, double-distilled water to make 100 ml.

Photo-Rex solution: Dissolve 2 g Photo-Rex [4-(methylamino)phenol sulfate] in a little silicic acid-free, double-distilled water. Add 17.5 g Sodium disulfite dry GR, and make up to 100 ml with silicic acid-free, double-distilled water.

This solution is only of limited stability.

Silicon standard solution: Make the contents of one ampoule of Silicon standard solution Titrisol® up to 1000 ml with silicic acid-free, double-distilled water. 1 ml ≙ 1 mg Si.

The dilutions necessary for plotting the reference curves are freshly prepared from this solution with silicic acid-free, double-distilled water using plastic pipettes.

When reporting the silicic acid concentration in mg/l SiO_2 care must be taken to convert silicon into silicon dioxide. 1 mg Si ≙ 2.139 mg SiO_2.

Reagents

Cat. No.		Packages
1182	Ammonium heptamolybdate (ammonium molybdate) GR	250 g, 1 kg, 5 kg
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
6258	Sodium disulfite dry GR	500 g, 1 kg, 5 kg
495	Oxalic acid GR	500 g, 1 kg, 5 kg
7299	Photo-Rex® [4-(methylamino)phenol sulfate]	250 g, 1 kg
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½
9947	Silicon standard solution Titrisol® 1.000 g ± 0.002 g Si ($SiCl_4$ in dil. NaOH)	1 amp.

Rapid photometric analysis possible with Spectroquant® Silicon
see Appendix

Silver

Qualitative analysis

10 ml of the water sample is treated in a test-tube with a few drops of Feigl's reagent, 5 ml diethyl ether superimposed, and the mixture shaken. In the presence of silver ions a reddish-brown film forms at the interface between the two phases. Lower limit of detection: about 0.4 mg/l.

Reagent preparation

Feigl's reagent: Dissolve 0.03 g 5-(4-Dimethylaminobenzylidene)rhodanine GR in 100 ml Acetone GR.

Reagents

Cat. Nr.		Packages
14	Acetone GR	1 l, 2½ l
921	Diethyl ether GR	1 l, 5 l
3059	5-(4-Dimethylaminobenzylidene)rhodanine GR (reagent for silver)	5 g

Rapid determination possible with Merckoquant® Test Strips
see Appendix

Quantitative analysis

Photometrically with dithizone

Suitable for determination of silver ions in concentrations from 0.05 to 1.50 mg/l Ag^+.

Interferences and pre-treatment

In order to achieve satisfactory results of measurement, all the apparatus should be cleaned extremely carefully before the determination by subjecting it to the action of Extran solution for one to two hours, and then rinsing successively with deionised water, dithizone solution, carbon tetrachloride and double-distilled water. To test for cleanness, 20 ml double-distilled water is introduced into the separating funnels before each determination, adjusted to pH about 9.5 with 1–2 drops of ammonia solution (0.91), and 0.5 ml dithizone solution added. After vigorous shaking for one minute the carbon tetrachloride phase should be colourless.

Interferences by zinc, cadmium and nickel ions in higher concentrations (> 100 mg/l) and by copper ions are eliminated by addition of 2 ml Titriplex III solution per sample volume.

In the presence of sulfide ions the sample is evaporated to dryness on a water bath with 1 ml nitric acid (about 1.40). The residue is moistened with 2 ml nitric acid (about 1.40), evaporated to dryness once again, and taken up in 50 ml double-distilled water, with heating.

The interference of organic substances and iron(III) ions is excluded by addition of hydroxylammonium chloride solution; this method is not applicable to solutions acidified with nitric acid. Larger amounts of organic constituents (potassium permanganate-consuming capacity > 25 mg/l) are decomposed by evaporation with sulfuric acid (about 1.55) and a few drops of nitric acid (about 1.40).

Procedure

Extreme care, and cleanness of apparatus, is necessary to avoid interferences; the determinations should always be carried out with the same cleaned apparatus.

Treat 100 ml test water in a 250-ml separating funnel with 15 ml nitric acid (about 1.035) or sulfuric acid (about 1.05), then with 50.0 ml dithizone solution, and shake vigorously for 5 min. If the carbon tetrachloride phase develops a golden yellow colour, a smaller starting volume of the test water should be taken. After complete separation of the phases, run the organic extract into a second separating funnel, treat with 10 ml ammonia solution (about 0.98), and shake for 2 min in a shaking machine. Dry the outlet tube of the separating funnel with a small roll of filter paper. Then allow some of the organic phase to run out in order to rinse the outlet tube. Filter the carbon tetrachloride layer through a plaited filter into a 1-cm cell, and measure at 470 nm against a blank treated in the same manner.

The reference curve is prepared from standard solutions of silver nitrate treated in the same manner as the water sample.

Calculation

The starting volume of the test water is to be taken into account in calculating the silver ion content in mg/l Ag^+.
1 mmol silver ions ≙ 107.88 mg Ag^+

Reporting of results

The values are rounded off to 0.01 mg/l for a silver ion content of less than 1 mg/l, and to 0.1 mg/l for 1 mg/l or more.

Reagent preparations

All the solutions are prepared with double-distilled water.

Ammonia solution (**about 0.98**): Mix 110 ml Ammonia solution min. 25% (0.91) Suprapur with 400 ml double-distilled water.

Dithizone solution: Dissolve about 12–13 mg Dithizone (1,5-diphenylthiocarbazone) GR in 100 ml Carbon tetrachloride GR (for determinations with dithizone). – Dilute 10 ml of this stock solution with 100 ml Carbon tetrachloride GR (for determination with dithizone). Only stable for about 1 day! – Store the solutions in brown bottles.

Extran solution: 2% aqueous solution of Extran MA 01 alkaline.

Hydroxylammonium chloride solution: Dissolve 20 g Hydroxylammonium chloride GR in 100 ml double-distilled water. The solution is stable for about 1 week.

Nitric acid (**about 1.035**): Mix 580 ml double-distilled water with 50 ml Nitric acid min. 65% (about 1.40) tested by the dithizone method GR.

Sulfuric acid (**about 1.55**): Carefully pour 350 ml Sulfuric acid 95–97% (about 1.84) GR into 310 ml double-distilled water.

Sulfuric acid (**about 1.05**): Mix 440 ml double-distilled water with 22 ml Sulfuric acid 95–97% (about 1.84) GR.

Silver standard solution: Treat 1.5746 g Silver nitrate GR with 10 ml nitric acid (1.035), and make up to 1000 ml with double-distilled water. 1 ml ≙ 1 mg Ag^+.
or:
Treat 1.4453 g Silver sulfate GR with 10 ml sulfuric acid (1.05), and make up to 1000 ml with double-distilled water. 1 ml ≙ 1 mg Ag^+.

The dilution solutions necessary for plotting of the reference curve are freshly prepared from one of these solutions.

Titriplex III solution: Dissolve 5 g Titriplex III GR in double-distilled water to make 100 ml.

Reagents

Cat.No.		Packages
9532	Alkalit® indicator strips pH 7.5–14.0 non-bleeding graduated in 0.5 pH units	1 pack
5428	Ammonia solution min. 25% (0.91) Suprapur®	250 ml, 1 l
3092	Dithizone (1,5-diphenylthiocarbazone) GR	5 g, 25 g, 100 g
7555	Extran® MA 01 alkaline	1 l, 5 l
4616	Hydroxylammonium chloride GR	100 g, 150 g, 1 kg
456	Nitric acid min. 65% (about 1.40) tested by the dithizone method GR	1 l, 2½ l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
1512	Silver nitrate GR	25 g, 100 g, 250 g, 1 kg
1509	Silver sulfate GR	25 g, 100 g
2208	Carbon tetrachloride GR (for determinations with dithizone)	1 l, 2½ l
8418	Titriplex® III [(ethylenedinitrilo)tetraacetic acid disiodium salt] (dihydrate) GR	100 g, 250 g, 1 kg, 5 kg

Solids content and loss on ignition

Determination of the total solids, dissolved solids, and loss on ignition

1. Total solids

(Sum of the non-volatile dissolved and undissolved substances contained in the water)

100 ml of unfiltered water is thoroughly shaken, and evaporated to dryness in an ignited and tared platinum dish with the aid of a surface evaporator, air or water bath. The residue is dried to constant weight in a drying chamber at 110° C, allowed to cool in a desiccator, and weighed. If the residue on drying is less than 20 mg/l, the determination is repeated with a larger volume of water.

2. Dissolved solids

(Amount of non-volatile dissolved substances in a water)

The water sample is filtered. If colloidally dissolved substances are not to be co-determined, a membrane filter is used for this purpose. 100 ml of the filtrate (in the case of a residue on drying of less than 20 mg/l, a larger volume of the water) is then treated as described under 1.

3. Loss on ignition

(The difference in weight between the dissolved solids and the residue on ignition)

The Residue on evaporation (dissolved solids) is ignited for 15 min at 600–650° C, thus charring the organic matter. If the ashing is still not complete – as detectable by brownish or black spots – the residue is moistened with a little ammonium nitrate solution, dried, and ignited again for 10 min at 600–650° C. Any dark colouration then remaining is attributable to inorganic constituents or to negligible residues of carbon. The residue is allowed to cool in a desiccator, weighed, and the weight subtracted from that of the dissolved solids to give the loss on ignition.

To determine the dissolved solids and loss on ignition of low-salt feed waters, completely desalted waters and condensates, initially larger volumes are concentrated by evaporation, and then treated further as described unter 2. and 3. The dissolved solids should not be below 0.5 mg/l starting volume.

Reporting of results

The values are rounded off to 1 mg/l, and the drying and ignition temperatures for the individual residues recorded.

Reagent preparation

Ammonium nitrate solution: Dissolve 1 g Ammonium nitrate GR in 100 ml deionised water.

Reagent

Cat.No.		Packages
1188	Ammonium nitrate GR	500 g, 1 kg, 5 kg

Sulfate

Qualitative analysis

The test water is filtered until clear if necessary, acidified in a test-tube with hydrochloric acid, and treated with a few drops of barium chloride solution. After heating, a white turbidity is produced either immediately or after a short interval depending on the content of sulfate ions.

Reagent preparation

Barium chloride solution: Dissolve 10 g Barium chloride GR in 90 ml deionised water. 1 ml of the solution precipitates about 40 mg SO_4^{2-}.

Reagents

Cat. No.		Packages
1719	Barium chloride GR	500 g, 1 kg, 5 kg
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l

Rapid determination possible with Merckoquant® Test Strips
see Appendix

Quantitative analysis

1. Gravimetrically as barium sulfate

Suitable for determination of sulfate ions in concentrations greater than about 100 mg/l SO_4^{2-}. In the case of lower concentrations the water sample is concentrated by evaporation before determination.

Interferences and pre-treatment

Interfering organic substances (corresponding to a potassium permanganate-consuming capacity greater than 30 mg/l) are eliminated by shaking the water with activated charcoal and then filtering through glass-fibre filters.

The interference can also be excluded by boiling the water sample for 10 min with excess potassium permanganate solution. The excess of potassium permanganate is then eliminated by dropwise addition of Perhydrol, and the solution filtered.

Iron ions in amounts greater than 1 mg/l Fe^{3+} are precipitated with excess ammonia solution after the treatment with Perhydrol, and filtered off.

Silicic acid interferes in contents greater than 25 mg/l SiO_2. For simultaneous elimination of silicic acid and organic substances the water is first evaporated almost to dryness in a platinum or quartz dish. The residue is evenly moistened with a few drops of hydrochloric acid and the same amount of sodium chloride solution, dried completely, and ashed. The residue on ignition is moistened with a little deionised water and a few drops of hydrochloric acid, and once again evaporated to dryness. The evaporation residue is taken up with deionised water and 1 ml hydrochloric acid, heated, and filtered. The filtration residue is washed with hot deionised water until the washings are free from chloride ions. The filtrate and washings are combined for the determination.

Procedure

Take 100 ml of the test water, pre-treated as appropriate, or a larger volume evaporated to 100 ml, neutralise if necessary, and add 1 ml hydrochloric acid. Heat the solution to boiling, treat dropwise with hot barium chloride solution to a slight excess, and keep at boiling point until the coarse-grained precipitate has settled. After cooling, filter off the precipitate through an ignited and tared porcelain filter crucible A 1, and wash with deionised water until the washings are free from chloride. Ignite the crucible at 700–800° C, allow to cool, and weigh.

Calculation

$1 \text{ mg } BaSO_4 \triangleq 0.4115 \text{ mg } SO_4^{2-}$

$$\text{mg/l } SO_4^{2-} = \frac{a \times 0.4115 \times 1000}{b}$$

a = weight in mg of $BaSO_4$ ignition residue
b = ml of test water used
1 meq sulfate ions ≙ 48 mg SO_4^{2-}
1 mmol sulfate ions ≙ 96.050 mg SO_4^{2-}

Reporting of results

The values are rounded off to 1 mg/l.

Reagent preparations

Barium chloride solution: Dissolve 10 g Barium chloride GR in 90 ml deionised water. 1 ml of this solution precipitates about 40 mg SO_4^{2-}.

Sodium chloride solution: Dissolve 10 g Sodium chloride cryst. GR in 100 ml deionised water.

Reagents

Cat. No.		Packages
2186	Charcoal activated GR	250 g, 1 kg
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
1719	Barium chloride GR	500 g, 1 kg, 5 kg
9935	Potassium permanganate solution 0.02 mol/l Titisol® concentrated solution for preparation of 1 litre of 0.1 N solution adjusted against oxalate	1 amp.
9122	Potassium permanganate solution 0.02 mol/l adjusted against oxalate	1 l
6404	Sodium chloride cryst. GR	500 g, 1 kg, 5 kg
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
7209	Perhydrol® 30% H_2O_2 GR	250 ml, 1 l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l

2. Titrimetrically by means of barium perchlorate solution with thorin as indicator

Suitable for determination of sulfate ions in concentrations from 12 to 1200 mg/l.

Interferences and pre-treatment

Cations are removed with a strongly acidic cation exchanger (see Procedure), as otherwise false results are obtained.

In the presence of sulfite and phosphate (e.g., in boiler water), which have an interfering effect, 25 ml of the water sample is pipetted into a 100-ml glass beaker. The sulfite is titrated with 0.005 mol/l iodine against 1 ml zinc iodide-starch solution as indicator. *10 drops of a 1% perchloric acid solution and 0.3 g magnesium hydroxide* carbonate are added, and the mixture kept gently boiling for 5 min. After cooling to 10° C, the mixture is filtered directly onto the ion-exchanger column, the filter washed with 4–5 ml cold deionised water, and this repeated a further three times, the washings being similarly passed into the column. The throughput is collected in a 50-ml volumetric flask, and made up to the mark with deionised water. 20 ml of this solution is mixed with 40 ml 2-propanol or ethanol, adjusted to a pH value of about 3.5 by addition of about 4–5 drops of 20% perchloric acid, and then treated as described under Procedure. The amount of sulfate arising in the iodometric determination of sulfite is subtracted from the total sulfate determined.

Procedure

Introduce 10 ml of the water sample with a sulfate content of 0.12–12.0 mg into a thin column of Ion exchanger I (strongly acidic cation exchanger). Then wash with 12–15 ml deionised water in four portions (the liquid should where possible run through as far as the upper limit of the column packing before the next portion of washing water is added). Collect the throughput in a 25-ml volumetric flask, and make up to the mark with deionised water. Pipette 10 ml of this solution into a conical flask, and add 40 ml 2-propanol or ethanol and about 4 drops of thorin solution as indicator. Adjust the pH to 2.5–4.0 with 20% perchloric acid, and titrate with 0.005 mol/l barium perchlorate *until the colour change from yellow to reddish-orange persists. It is advisable to* undertake a colour comparison for exact detection of the change in the indicator. The major part of the barium perchlorate solution should be added rapidly, but there should be an interval of 2–3 seconds before addition of the last drops.

Calculation

1 ml 0.005 mol/l barium perchlorate $\triangleq$ 0.48 mg SO_4^{2-}.

The starting volume of water and the amount of water employed for the titration after the treatment with the cation exchanger are to be taken into account in the calculation.

In the presence of sulfite the amount of sulfate arising in the iodometric determination of sulfite is subtracted from the sulfate determined (see Interferences and pre-treatment).

Reporting of results

The values are rounded off to 1 mg/l.

Reagent preparations

Iodine 0.005 mol/l: Dilute 200 ml 0.05 mol/l Iodine solution to 1000 ml with deionised water.

Perchloric acid (about 1%): Dilute 1 ml Perchloric acid about 60% (about 1.53) GR to 100 ml with deionised water.

Perchloric acid (about 20%): Dilute 22 ml Perchloric acid about 60% (about 1.53) GR to 100 ml with deionised water.

Thorin solution: Dissolve 0.2 g Thorin indicator for sulfate titration with barium perchlorate in deionised water, and make up to 100 ml.

Reagents

Cat. No.		Packages
972	Ethanol (ethyl alcohol) absolute GR	1 l, 2½ l
9086	Barium perchlorate solution 0.005 mol/l in 2 propanol/water	1 l
5257	Ion exchanger Merck Lewatit® S 1080 0.1–0.25 mm (60–150 mesh ASTM) strongly acidic cation exchanger Na^+ form GR ® = trade mark of Bayer AG	100 ml, 500 ml
4765	Ion exchanger I (strongly acidic cation exchanger)	100 g, 500 g
9099	Iodine solution 0.05 mol I_2/l	1 l
9910	Iodine solution 0.05 mol I_2/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
5827	Magnesium hydroxide carbonate GR	100 g, 250 g, 1 kg
518	Perchloric acid about 60% (about 1.53) GR	500 ml, 1 l, 2½ l
9634	2-Propanol (iso-propyl alcohol) GR	1 l, 2½ l
9531	Acilit® indicator strips pH 0–6.0 non-bleeding graduated in 0.5 pH units	1 pack
8294	Thorin [1-(2-arsonophenylazo)-2-hydroxy-3,6-naphthalenedisulfonic acid sodium salt] indicator for sulfate titration with barium perchlorate	5 g
9535	Universal indicator strips pH 0–14.0 non-bleeding	1 pack
5445	Zinc iodide-starch solution	500 ml

Sulfide

Qualitative analysis

1. Alkali, earth alkali and some metallic sulfides, particularly iron sulfide, may be detected by the characteristic odour resulting from evolution of hydrogen sulfide on acidification of the water sample with hydrochloric acid.

2. A moistened lead acetate paper is suspended in a closed flask in the atmosphere above the test water. On acidification with hydrochloric acid the paper develops a brown colour either immediately or on gentle heating, when the above-mentioned sulfides are present. Heavy metal sulfides such as copper, nickel or lead sulfide are only decomposed with difficulty by hydrochloric acid or not at all. When the latter are present, sulfur separates out on addition of nitric acid and heating.

Reagents

Cat. No.		Packages
9511	Lead(II) acetate paper	1 pack
454	Nitric acid min. 65% (about 1.40) GR	1 l, 2½ l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l

Rapid determination possible with Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative analysis

1. Titrimetrically after precipitation as cadmium sulfide

Suitable for determination of sulfide ions in concentrations greater than 2 mg/l S^{2-}. Only sulfides decomposable by hydrochloric acid are determined (see under Qualitative analysis).

Interferences and pre-treatment

Organic substances adsorbed by cadmium sulfide and asbestos interfere (see under Procedure).

Hydrogen sulfide is eliminated by passing through nitrogen in the cold (Procedure b). An exact separation of hydrogen sulfide and sulfide ions is, however, not possible.

If the total content of hydrogen sulfide and sulfide ions is to be determined, the above gassing of the water sample with nitrogen is omitted.

Procedure

a) In the absence of larger amounts of adsorbable organic substances and free hydrogen sulfide.

Fill a glass-stoppered bottle of known capacity to overflowing with the test water. Add 5 ml cadmium acetate solution with a pipette, close the bottle avoiding the inclusion of air bubbles, and shake well. Allow to stand for at least 5 hours, then filter the cadmium sulfide precipitate over asbestos, and wash with deionised water. Transfer the asbestos and precipitate to a conical flask, add excess 0.005 mol/l iodine (50 ml or more), and acidify with 20 ml phosphoric acid. After 20 min back-titrate the excess iodine with 0.01 mol/l sodium thiosulfate using zinc iodide-starch solution as indicator.

Calculation

1 ml 0.005 mol/l iodine $\triangleq$ 0.1603 mg S^{2-}

$$\text{mg/l } S^{2-} = \frac{(a - b) \times 0.1603 \times 1000}{c - 5}$$

a = ml 0.005 mol/l iodine added
b = ml 0.01 mol/l sodium thiosulfate consumed
c = capacity in ml of the glass-stoppered bottle
1 meq sulfide ions $\triangleq$ 16.03 mg S^{2-}
1 mmol sulfide ions $\triangleq$ 32.06 mg S^{2-}

b) In the presence of larger amounts of adsorbable organic substances and/or free hydrogen sulfide.

The apparatus required consists of a distillation flask with separating funnel attached and connected to a bulb-tube washer, and having a gas inlet tube connected to a cylinder of nitrogen via a gas-washing bottle. The gas-washing bottle should contain about 100 ml nitrogen-purifying solution.

Charge the distillation flask with 200 ml of the test water, or with a larger volume depending on the concentration. Expel the oxygen and any free hydrogen sulfide present from the apparatus by passing through nitrogen. Interrupt the flow of nitrogen, *introduce 20–30 ml cadmium acetate solution into the bulb-tube washer*, and then add 50 ml hydrochloric acid to the distillation flask. The hydrogen sulfide liberated from the sulfides or hydrogen sulfides is collected in the cadmium acetate solution. When decomposition is complete, expel the remaining hydrogen sulfide quantitatively into the washer by passing through nitrogen and gentle heating. After not less than 5 hours, filter the cadmium sulfide precipitate over asbestos, wash with deionised water, dissolve in excess 0.005 mol/l iodine (50 ml or more) in a conical flask, and acidify with phosphoric acid. After 20 min back-titrate the excess iodine with 0.01 mol/l sodium thiosulfate using zinc iodide-starch solution as indicator.

For determination of the total concentration of free hydrogen sulfide and sulfide ions the apparatus is initially freed from oxygen to a large extent by passing through nitrogen. The bulb-tube washer is then charged with the cadmium acetate solution, and the distillation flask with the water sample and the hydrochloric acid through the separating funnel. The subsequent procedure is as described above.

Calculation

1 ml 0.005 mol/l iodine ≙ 1.1603 mg S^{2-}

$$\text{mg/l } S^{2-} = \frac{(a - b) \times 0.1603 \times 1000}{c}$$

a = ml of 0.005 mol/l iodine added
b = ml of 0.01 mol/l sodium thiosulfate consumed
c = ml of test water used
1 meq sulfide ions ≙ 16.03 mg S^{2-}
1 mmol sulfide ions ≙ 32.06 mg S^{2-}

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Cadmium acetate solution: Dissolve 5 g Cadmium acetate GR in 30 ml Acetic acid glacial min. 96% (about 1.06) GR and 65 ml deionised water.

Iodine 0.005 mol/l: Dilute 100 ml Iodine solution to 1000 ml with boiled deionised water as required.

Sodium thiosulfate 0.01 mol/l: Make 100 ml 0.1 mol/l Sodium thiosulfate solution up to 1000 ml with boiled deionised water as required.

Phosphoric acid: Dilute 124 ml ortho-Phosphoric acid min. 85% (about 1.71) GR with 500 ml deionised water.

Nitrogen-purifying solution: Dissolve 5 g Mercury(II) chloride GR in potassium permanganate solution (2 g Potassium permanganate dissolved in 100 ml deionised water) to make 100 ml.

Reagents

Cat. No.		Packages
1560	Asbestos for Gooch crucibles (LAB)	50 g, 250 g, 1 kg
2003	Cadmium acetate GR	100 g, 500 g
62	Acetic acid glacial min. 96% (about 1.06) Gr	1 l, 2½ l
9910	Iodine solution 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9099	Iodine solution 0.05 mol/l	1 litre
5082	Potassium permanganate GR	250 g, 1 kg, 5 kg
9950	Sodium thiosulfate 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	1 l
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
4419	Mercury(II) chloride GR	50 g, 250 g, 1 kg
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
823 314	Nitrogen	0.44 l
5445	Zinc iodide-starch solution	500 ml

2. Photometrically via methylene blue

Suitable for determination of sulfide ions in concentrations from 0.02–20 mg/l S^{2-}.

Interferences and pre-treatment

Some strongly reducing constituents can interfere by diminishing the intensity of the colour.

Sulfites affect the determination in concentrations greater than 200 mg/l SO_3^{2-}, thiosulfates in concentrations greater than 5 mg/l $S_2O_3^{2-}$; the interference of concentrations up to 0.5 mg/l NO_2^- can be excluded by the action of 3 drops of urea solution in the starting volume.

In the case of concentrations of mineral substances above about 100 mg in the starting volume, a diminution of colour is to be expected. When the sulfide ion content is sufficiently high, a dilution of the water sample or a distillation prior to the determination is advisable.

Procedure

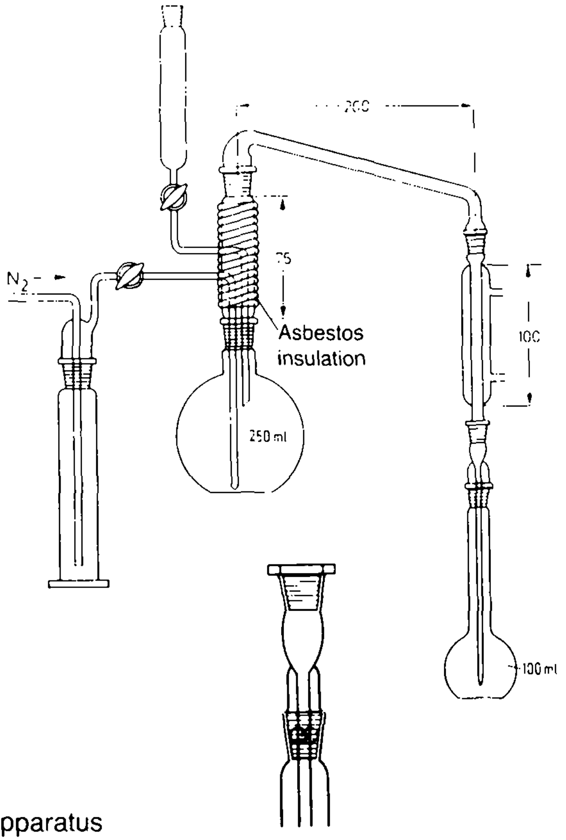
2.1. Direct determination without distillation

Charge a 100-ml volumetric flask with 10 ml zinc acetate solution. Depending on the content of sulfide ions to be expected, add up to 75 ml of the water sample with a pipette at the site of sampling, and – if necessary – sufficient deionised water that the level of the liquid is still somewhat below the shoulder of the flask. Close the flask with a ground-glass stopper. In the laboratory introduce a layer of 10 ml N,N-dimethyl-1,4-phenylenediammonium dichloride solution under the liquid. Close the flask, shake briefly, and immediately add 0.5 ml ammonium iron(III) sulfate solution with a pipette. Shake vigorously once again, allow the flask to stand for 10 min at room-temperature, and then make up to the mark with deionised water. Measure at 670 nm against deionised water in 1-cm cells. In the case of sulfide ion concentrations below 5 μg S^{2-} use 5-cm cells.

The reference curve is prepared from a standard solution of zinc sulfide. Depending on the iodometrically determined sulfide ion content in this solution, varying volumes containing between 0.5–70 μg S^{2-} are pipetted into 100-ml volumetric flasks and treated in the same manner as the test water.

2.2. Determination with distillation

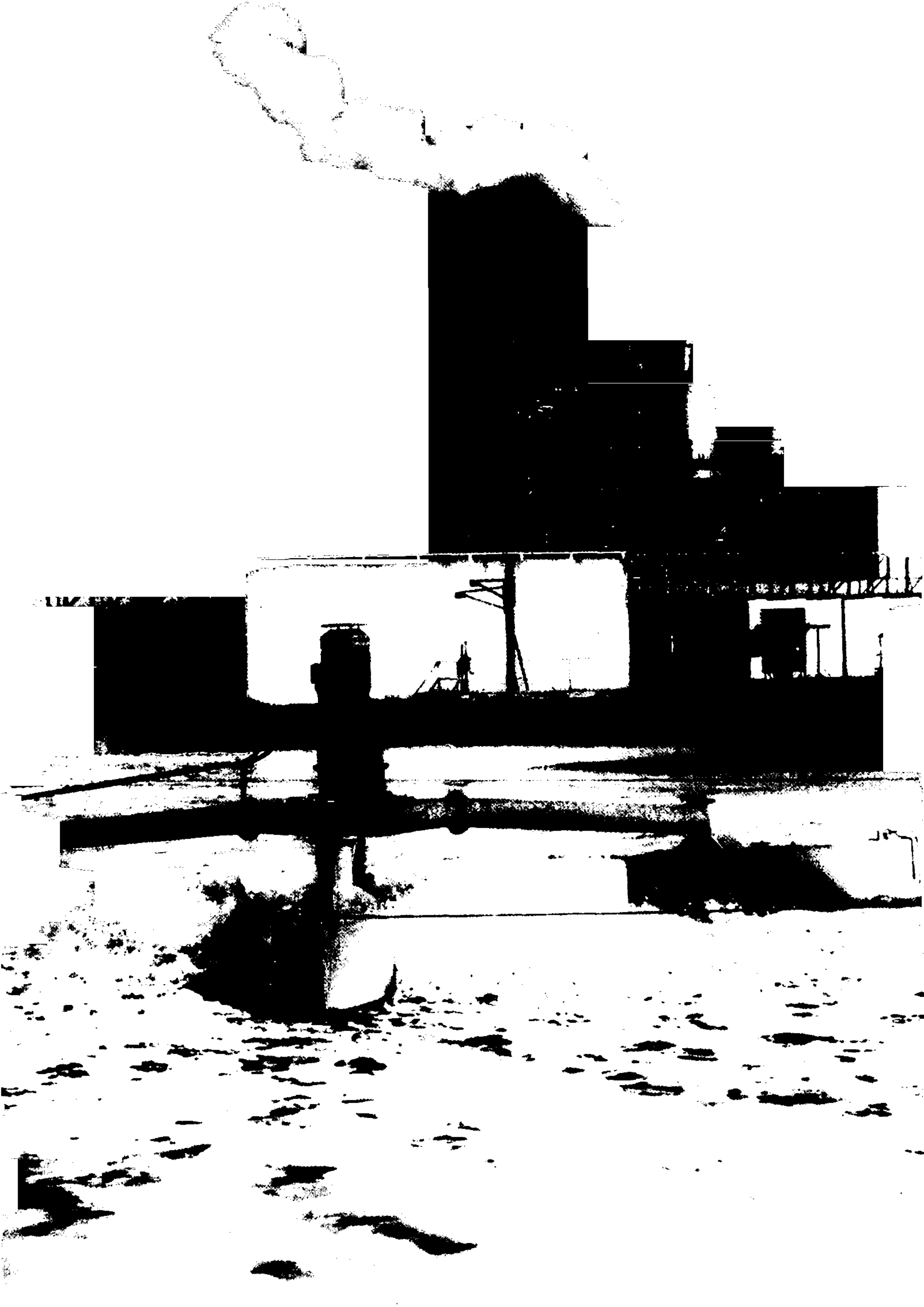
The distillation is carried out in an apparatus as shown in the drawing on page 192:



Distillation apparatus

No rubber connections may be used in setting up the apparatus.

Charge the 250-ml distillation flask with 10 ml zinc acetate solution. Depending on the content of sulfide ions to be expected, add up to 150 ml of the water sample with a pipette at the site of sampling, and close the flask with a ground-glass stopper. In the laboratory connect the flask to the distillation apparatus. Introduce 10 ml zinc acetate solution into the 100-ml volumetric flask with bore serving as receiver (see drawing of flask neck). The ground-glass inlet tube with bore must dip into the solution. The bores in the volumetric flask and the inlet tube are made to coincide by turning. Heat to



boiling under a moderate flow of nitrogen which has passed through a washing bottle with nitrogen-purifying solution. When water is already distilling over into the receiver, add 5 ml phosphoric acid to the distillation flask through the dropping funnel. After 15 min, when the volume of liquid in the receiver is about 60 ml, cease distillation. Remove volumetric flask and inlet tube from the apparatus. Insert a layer of 10 ml N,N-dimethyl-1,4-phenylenediammonium dichloride below the liquid through the inlet tube. Shake gently, and immediately add 0.5 ml ammonium iron(III) sulfate solution with a pipette. Separate the bores of the two ground-glass joints by turning, and close the flask and inlet tube with a ground-glass stopper. Shake well, remove the inlet tube, and rinse with deionised water. Allow the flask to stand for 10 min at room-temperature, and then make up to the mark with deionised water. Measure at 670 nm against deionised water in 1-cm cells. In the case of sulfide ion contents below 5 μg S^{2-}, use 5-cm cells.

The reference curve is prepared as described under 2.1.

Calculation

The starting volume of the water sample is to be taken into account in calculation of the sulfide ion content in μg or mg/l S^{2-} after reading off the absolute amount from the reference curve.

1 meq sulfide ions ≙ 16.03 mg S^{2-}
1 mmol sulfide ions ≙ 32.06 mg S^{2-}

Reporting of results

The values are rounded off to 0.01 mg/l.

Reagent preparations

Ammonium iron(III) sulfate solution: Pour 10 ml Sulfuric acid 95–97% (about 1.84) GR over 50 g Ammonium iron(III) sulfate GR in a 500-ml volumetric flask, and make up to the mark with water.

N,N-Dimethyl-1,4-phenylenediammonium dichloride solution: Slurry 2 g N,N-Dimethyl-1,4-phenylenediammonium dichloride GR in a 1000-ml volumetric flask with 200 ml deionised water. Carefully add 200 ml Sulfuric acid 95–97% (about 1.84) GR, and after cooling make up to the mark with deionised water.

Urea solution: Dissolve 5 g Urea GR in 95 ml deionised water.

Nitrogen-purifying solution: Dissolve 5 g Mercury(II) chloride GR in potassium permanganate solution (2 g Potassium permanganate GR dissolved in 100 ml deionised water) to make 100 ml.

Sulfide standard solution: (Boiled, double-distilled water is to be used for all the solutions). Mix 250 ml zinc acetate solution with 500 ml of a freshly prepared gelatin solution (150 mg Gelatin for microbiology dissolved in 500 ml deionised water), and place in a brown glass bottle as receiver under the distillation apparatus (see drawing). The outlet tube of the condenser must dip deeply into the solution. Heat 150 ml boric acid solution (6 g Boric acid cryst. GR dissolved in 150 ml warm water) to boiling in the distillation flask under a moderate flow of nitrogen which has passed through the nitrogen-purifying solution in the washing bottle. When the boric acid solution is boiling and water is already distilling over, slowly add sodium sulfide solution [a washed crystal of Sodium sulfide GR (about 40 mg ≙ 5 mg S^{2-}) dissolved in a little deionised water] through the dropping funnel. After 15 min the liberated hydrogen sulfide has distilled off, and is bound as zinc sulfide in the receiver. Make the liquid up to 1000 ml with deionised water, and store in a brown glass bottle. Any flocculations can be filtered off. The sulfide ion content of this solution is determined iodometrically in accordance with 1.

Zinc acetate solution: Dissolve 2 g Zinc acetate GR in deionised water to make 100 ml.

Reagents

Cat. No.		Packages
3776	Ammonium iron(III) sulfate GR	500 g, 1 kg, 5 kg
165	Boric acid cryst. GR	500 g, 1 kg, 2½ kg
3067	N,N-Dimethyl-1,4-phenylenediammonium dichloride GR	25 g, 100 g
4070	Gelatin for microbiology	100 g, 500 g
8487	Urea GR	500 g, 1 kg, 5 kg
5082	Potassium permanganate GR	250 g, 1 kg, 5 kg
6638	Sodium sulfide GR	250 g, 1 kg
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
4419	Mercury(II) chloride GR	50 g, 250 g, 1 kg
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
8802	Zinc acetate GR	250 g, 1 kg

Rapid photometric analysis possible with Spectroquant® Hydrogen Sulfide
see Appendix

Sulfite

Qualitative analysis

1. The water sample is acidified in a narrow-necked flask with phosphoric acid, and the opening covered with a moistened strip of freshly prepared potassium iodate-starch paper. In the presence of sulfite ions the paper turns blue immediately or after gentle heating. At higher concentrations the blue colour disappears under further reduction of the primarily separated iodine to hydrogen iodide; sulfur dioxide can be perceived from the odour.

Reagent preparation

Potassium iodate-starch paper: Impregnate strips of filter paper with potassium iodate solution and starch solution, and dry.

Reagents

Ca. No.		Packages
5051	Potassium iodate GR	100 g, 500 g
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
1252	Starch soluble GR	100 g, 250 g, 1 kg

2. Boedeke's reaction

The test water is neutralised if necessary, and treated with sodium nitroprusside solution. In the presence of sulfite ions a faint pink colour is produced which changes to a marked red on addition of plenty of zinc sulfate. The reaction is even more sensitive after additon of a little potassium hexacyanoferrate(II).

Reagent preparation

Sodium nitroprusside solution: Dissolve 1 g Sodium nitroprusside GR in 100 ml deionised water.

Reagents

Cat. No.		Packages
4984	Potassium hexacyanoferrate(II)	500 g
9533	Neutralit® indicator strips pH 5.0–10.0 non-bleeding graduated in 0.5 pH units	1 pack
6541	Sodium nitroprusside GR	25 g, 100 g, 500 g
8883	Zinc sulfate 7-hydrate GR	500 g, 1 kg, 5 kg

Rapid determination possible with Merckoquant® Test Strips
see Appendix

Quantitative analysis

1. Titrimetrically by means of iodine solution

Suitable for determination of sulfite ions in concentrations greater than 2 mg/l SO_3^{2-}.

Interferences and pre-treatment

All substances oxidisable by iodine, such as nitrite and sulfide ions, and larger amounts of organic substances, interfere.

Nitrite ions are determined separately beforehand, and taken into account in the calculation. Similarly with sulfide ions and any free hydrogen sulfide present.

In the presence of larger amounts of organic substances the gravimetric determination in accordance with 3. is to be recommended.

Procedure

Care should be taken during sampling that as little air as possible comes into contact with the test water. It is similarly advisable in the titration to use a vessel with a cover through which the outlet of the burette dips into the liquid being titrated.

Introduce 50 ml test water, 1 ml sulfuric acid and a magnetic stirring rod (with plastic envelope) into the titration vessel, and place on a magnetic stirrer. Add 1 ml zinc iodide-starch solution, and titrate with 0.05 mol/l or 0.005 mol/l iodine depending on the concentration of sulfite ions, at constant stirring speed and avoiding air eddies. The end-point is detectable by a faint, persistent blue colour.

Calculation

1 ml 0.05 mol/l iodine $\triangleq$ 4.003 mg SO_3^{2-}
1 ml 0.005 mol/l iodine $\triangleq$ 0.400 mg SO_3^{2-}

$$\text{mg/l } SO_3^{2-} = \frac{a \times 4.003 \times 1000}{b} \text{ or } = \frac{a' \times 0.400 \times 1000}{b}$$

a = ml of 0.05 mol/l iodine consumed
a' = ml of 0.005 mol/l iodine consumed
b = ml of test water used
1 meq sulfite ions $\triangleq$ 40.03 mg SO_3^{2-}
1 mmol sulfite ions $\triangleq$ 80.058 mg SO_3^{2-}

Reporting of results

The values are rounded off to 1 mg/l.

Reagent preparations

Sulfuric acid: Carefully stir 1 part by volume Sulfuric acid 95–97% (about 1.84) GR into 1 part by volume deionised water.

Iodine 0.005 mol/l: Dilute 100 ml 0.05 mol/l Iodine solution to 1000 ml with boiled deionised water as required.

Reagents

Cat. No.		Packages
9910	Iodine solution 0.05 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9099	Iodine solution 0,05 mol/l	1 l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
5445	Zinc iodide-starch solution	500 ml

2. Titrimetrically by means of iodine solution

Suitable for determination of sulfite ions in concentrations greater than 0.1 mg/l SO_3^{2-}.

Interferences and pre-treatment

As described under 1.

Procedure

Fill a glass-stoppered bottle of known capacity (oxygen-determination bottle, 200–300 ml) with the test water by introducing the water slowly through a glass tube reaching almost to the bottom of the bottle and allowing to overflow for 10 min. Then withdraw the inlet tube without interrupting the flow of water. Depending on the sulfite ion content add 10–30 ml 0.05 mol/l iodine and 3 ml phosphoric acid by means of oxygen-determination pipettes. Close the bottle, avoiding the formation of air bubbles, and shake well. After 10 min transfer quantitatively to a 500-ml conical flask, and back-titrate the excess iodine with 0.1 mol/l sodium thiosulfate against zinc iodide-starch solution as indicator. If the consumption of 0.05 mol/l iodine is less than 1 ml, repeat the determination with 0.005 mol/l iodine and 0.01 mol/l sodium thiosulfate under the same conditions.

Calculation

1 ml 0.05 mol/l iodine ≙ 4.003 mg SO_3^{2-}
1 ml 0.005 mol/l iodine ≙ 0.400 mg SO_3^{2-}

$$\text{mg/l } SO_3^{2-} = \frac{(a-b) \times 4.003 \times 1000}{c-(a+3)} \quad \text{or} \quad \frac{(a'-b') \times 0.400 \times 1000}{c-(a'+3)}$$

a = ml of 0.05 mol/l iodine added
a' = ml of 0.005 mol/l iodine added
b = ml of 0.1 mol/l sodium thiosulfate consumed
b' = ml of 0.01 mol/l sodium thiosulfate consumed
c = volume of the bottle in ml
1 meq sulfite ions ≙ 40.03 mg SO_3^{2-}
1 mmol sulfite ions ≙ 80.058 mg SO_3^{2-}

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Iodine 0.005 mol/l: Dilute 100 ml 0.05 mol/l Iodine solution to 1000 ml with boiled deionised water as required.

Sodium thiosulfate 0.01 mol/l: Make 100 ml 0.1 mol/l Sodium thiosulfate solution up to 1000 ml with boiled deionised water as required.

Phosphoric acid (about 1.15): Mix 12.5 ml ortho-Phosphoric acid min. 85% (about 1.71) GR with 100 ml deionised water.

Reagents

Cat. No.		Packages
9910	Iodine solution Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9099	Iodine solution 0.05 mol/l	1 l
9950	Sodium thiosulfate solution 0.1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.1 N solution	1 amp.
9147	Sodium thiosulfate solution 0.1 mol/l	1 l
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
5445	Zinc iodide-starch solution	500 ml

3. Gravimetrically as barium sulfate

Suitable for determination of higher concentrations of sulfite ions and in the presence of larger amounts of organic substances (more than 60 mg $KMnO_4$-consuming capacity/l).

Procedure

Use a distillation apparatus with an extended condenser end.

Before introducing the test water into the distillation flask fill the apparatus with nitrogen or carbon dioxide to prevent oxidation of the sulfur dioxide, with the lower end of the condenser dipping into iodine-potassium iodide solution (in excess). Depending on the sulfite ion concentration, introduce 300–500 ml of the water sample into the distillation flask, add 20 ml phosphoric acid, and distill over about 200 ml. Then treat the liquid in the receiver with 1 ml hydrochloric acid, heat to boiling, and precipitate the sulfate formed as barium sulfate by addition of an excess of hot barium chloride solution. Allow to stand over night, filter the precipitate over a hard filter paper, and wash free from acid with hot deionised water. Dry, ash in a tared crucible, and ignite at 800° C.

Calculation

1 mg $BaSO_4 \triangleq 0.343$ mg SO_3^{2-}

$$\text{mg/l } SO_3^{2-} = \frac{a \times 0.343 \times 1000}{b}$$

a = mg $BaSO_4$ ignition residue
b = ml of test water used
1 meq sulfite ions $\triangleq$ 40.03 mg SO_3^-
1 mmol sulfite ions $\triangleq$ 80.058 mg SO_3^{2-}

Reporting of results

The values are rounded off to 1 mg/l.

Reagent preparations

Barium chloride solution: Dissolve 12.5 g Barium chloride GR in 500 ml deionised water.

Iodine-potassium iodide solution: Dissolve 7.5 g Potassium iodide GR and 5 g Iodine resublimed GR in that order in 500 ml deionised water. Dilute the solution to 100 ml.

Phosphoric acid (about 1.15): Dilute 12.5 ml ortho-Phosphoric acid min. 85% (about 1.71) GR with 100 ml deionised water.

Hydrochloric acid (about 1.05): Mix 75 ml Hydrochloric acid fuming min. 37% (about 1.19) GR with 200 ml deionised water.

Reagents

Cat. No.		Packages
1719	Barium chloride GR	500 g, 1 kg, 5 kg
4761	Iodine resublimed GR	100 g, 500 g, 1 kg
5043	Potassium iodide neutral GR	250 g, 1 kg, 2½ kg
573	ortho-Phosphoric acid min. 85% (about 1.71) GR	1 l, 2½ l
317	Hydrochloric acid fuming min. 37% (about 1.19) GR	1 l, 2½ l

Thiocyanate

Qualitative analysis

1. The water sample is acidified with hydrochloric acid, and treated with a few drops of iron(III) chloride solution. In the presence of thiocyanate ions a pink to red colour is produced depending on the concentration.

The alkali salts of acetic acid, mercury(II) chloride, nitrous acid, and phosphoric acid and fluoride ions in sufficient amount, interfere. In all cases the red colour more or less disappears.

2. For specific detection in the presence of cyanide ions see under "Cyanide, Qualitative analysis".

Reagent preparation

Iron(III) chloride solution: Dissolve 2 g Iron(III) chloride GR in 100 ml deionised water.

Reagents

Cat. No.		Packages
3943	Iron(III) chloride GR	250 g, 1 kg
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l

Quantitative analysis

Photometrically as iron(III) thiocyanate

Suitable for determination of thiocyanate ions in concentrations between 0.2 and 300 mg/l CNS^-.

Interferences and pre-treatment

Oxalate ions in concentrations greater than 50 mg/l and fluoride ions greater than 2 mg/l yield low results for the thiocyanate ions.

Interferences by sulfide ions, thiosulfate ions, colloidal turbidity, etc. are excluded by addition of zinc chloride solution and subsequent filtration of the precipitate (see Procedure).

Procedure

Treat 100 ml test water, or a smaller volume depending on the thiocyanate concentration, with 10 ml zinc chloride solution, and make up to 200 ml with deionised water. Allow to stand for a short time, and filter off the resulting precipitate.

Add 2 ml hydrochloric acid and 2 ml iron(III) chloride solution to the filtrate. After 5 min measure at 475 nm against a blank prepared from 100 ml deionised water, 5 ml zinc chloride solution, 2 ml hydrochloric acid and 2 ml iron(III) chloride solution.

The reference curve is prepared from standard solutions of potassium thiocyanate treated in the same manner as the water sample.

Calculation

The actual starting volume of water sample which was made up to 200 ml with deionised water is to be taken into account in the calculation.

1 mmol thiocyanate ions ≙ 58.08 mg CNS^-

Reporting of results

The values are rounded off to 0.1 mg/l.

Reagent preparations

Iron(III) chloride solution: Dissolve 2 g Iron(III) chloride GR in 100 ml deionised water.

Thiocyanate standard solution: Dissolve 1.6732 g Potassium thiocyanate GR in deionised water, and make the solution up to 100 ml. 1 ml ≙ 1 mg CNS^-.
The dilutions necessary for plotting of the reference curve are prepared from this solution.

Zinc chloride: Dissolve 37 g Zinc chloride dry GR in 100 ml deionised water.

Reagents

Cat. No.		Packages
3943	Iron(III) chloride GR	250 g, 1 kg
5125	Potassium thiocyanate GR	250 g, 1 kg, 5 kg
316	Hydrochloric acid min. 25% (about 1.125)	1 l, 2½ l
8816	Zinc chloride GR	250 g, 1 kg, 5 kg

Zinc

Qualitative analysis

The green solution of dithizone in carbon tetrachloride turns a purplish-red on shaking with zinc solutions. Interfering heavy metals are masked with sodium thiosulfate.

About 50 ml of the water sample is acidified with a few drops of hydrochloric acid, and treated with sodium acetate solution until a pH of about 5 is obtained. 3 ml sodium thiosulfate solution is then added, and the solution shaken vigorously with 3 ml dithizone solution. A red colour is produced by extremely small amounts of zinc.

Reagent preparations

Dithizone solution: Dissolve 10 mg Dithizone GR in 400 ml Carbon tetrachloride GR.

Sodium acetate solution: Dissolve 20 g Sodium acetate cryst. GR in 80 ml deionised water.

Sodium thiosulfate solution: Dissolve 50 g Sodium thiosulfate 5-hydrate GR in 30 ml deionised water.

Reagents

Cat. No.		Packages
3092	Dithizone (1,5-diphenylthiocarbazone) GR	5 g, 25 g, 100 g
6267	Sodium acetate cryst. GR indifferent to potassium permanganate	500 g, 1 kg, 5 kg
6516	Sodium thiosulfate 5-hydrate GR	500 g, 1 kg, 5 kg
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
9542	Special indicator strips pH 4.0–7.0 non-bleeding graduated in 0.2–0.3 pH units	1 pack
2208	Carbon tetrachloride GR (for determinations with dithizone)	1 l, 2½ l

Rapid determination possible with Merckoquant® Test Strips and with Aquaquant® and Microquant® Reagent Kits

see Appendix

Quantitative analysis

Photometrically with dithizone

Suitable for determination of zinc ions in concentrations less than 20 mg/l Zn^{2+}.

Interferences and pre-treatment

Dithizone is not a specific reagent for zinc. In the pH range 4–7 the following elements are extractable: Au, Ag, Pd, Hg, In, Cu, Bi,. Ni, Co, Zn, Cd, Pb, Tl. These elements can be masked to a large extent by addition of sodium thiosulfate and potassium cyanide for the determination, thus leaving the method practically specific for zinc ions.

Interfering organic substances are eliminated by evaporation to dryness and subsequent gentle ignition (at 650°) of a measured amount of water. The residue is taken up with as little 2 mol/l hydrochloric acid as possible, diluted with deionised water, and boiled for a short time.

In order to bring undissolved zinc compounds into solution, the measured amount of water is boiled for a short time with addition of 1–3% hydrochloric acid (about 1.125).

All the glass apparatus used should be rinsed out with carbon tetrachloride before use; in no case should domestic detergents be used.

Procedure

To the pre-treated, boiled water add sufficient sodium acetate solution to bring the pH value to 5. Transfer the solution, whose zinc ion content should be between 5 and 50 μg Zn^{2+}, quantitatively to a separating funnel, add 20 ml masking solution, and mix well. Add 5 ml dithizone solution, and shake vigorously for 5 min. If the carbon tetrachloride layer exhibits a red to reddish-violet colour, repeat the extraction with a smaller volume of water. After separation of the layers, run the lower phase into a second separating funnel, add 10 ml sodium phosphate-sodium sulfide solution and 15 ml deionised water, and shake well for ½ min. Dry the outlet tube of the separating funnel with a small roll of filter paper, and wash with a little of the carbon tetrachloride layer. Fill a 0.5-cm cell with the organic phase, which contains all the zinc as zinc dithizonate. Measure at 538 nm against a blank treated in the same manner.

The reference curve is prepared from standard solutions of dissolved zinc or dilution solutions of Zinc standard solution Titrisol treated in the same manner as the water sample.

Calculation

The zinc ion content in mg/l Zn^{2+} is calculated from the volume of water used and the absolute amount of zinc ascertained from the reference curve.

Reporting of results

The values are rounded off to 0.01 mg/l for a zinc ion content less than 1 mg/l, to 0.1 mg/l for 1–10 mg/l, and to 1 mg/l for more than 10 mg/l.
1 meq zinc ions ≙ 32.69 mg Zn^{2+}
1 mmol zinc ions ≙ 65.37 mg Zn^{2+}

Reagent preparations

All the aqueous solutions are prepared with zinc-free deionised water.

Dithizone solution: Dissolve 25 mg Dithizone (1,5-diphenylthiocarbazone) GR in 200 ml Carbon tetrachloride GR (for determination with dithizone).

Dilute 50 ml of this stock solution to 250 ml with Carbon tetrachloride GR (for determinations with dithizone).

Store the solutions in brown bottles.

Sodium acetate solution: Dissolve 10 g Sodium acetate cryst. GR indifferent to potassium permanganate in 90 ml deionised water.

Sodium phosphate-sodium sulfide solution:

Solution a: Dissolve 60 g di-Sodium hydrogen phosphate 12-hydrate GR in 1000 ml deionised water. Adjust the solution to pH 11.0 with an approx. 5 mol/l solution of sodium hydroxide (200 g Sodium hydroxide pellets GR dissolved in deionised water to make 1000 ml).

Solution b: Pass hydrogen sulfide into a 0.25 mol/l solution of sodium hydroxide until pH 8.0 is attained. Always prepare the solution fresh.

Mix 100 ml Solution a with 10 ml Solution b as required.

Hydrochloric acid 2 mol/l: Dilute the contents of one ampoule of 1 mol/l Hydrochloric acid Titrisol concentrated solution for preparation of 1 litre of 1 N solution to 500 ml with deionised water.

Making solution:

Solution a: Dissolve 0.15 g Ammonium oxalate GR, 1.5 g Potassium cyanide GR and 24.0 g Sodium acetate cryst. GR indifferent to potassium permanganate in 200 ml deionised water. Then add 10 ml approx. 2 mol/l ammonia (150 ml Ammonia solution min. 25% (0.91) GR made up to 1000 ml with deionised water) and 70 ml 1 mol/l Hydrochloric acid.

Solution b: Dissolve 120 g Sodium thiosulfate 5-hydrate GR in 200 ml deionised water.

When required, add Solution a to Solution b, and make the mixture up to 1000 ml with deionised water.

Zinc standard solution: Dissolve 4.399 g Zinc sulfate GR in deionised water, and make up to 1000 ml. 1 ml ≙ 1 mg Zn^{2+}.

Zinc standard solution: Dissolve 1000 mg Zinc granular GR in 10 ml nitric acid (about 1.20) (1 part by volume Nitric acid 65% [about 1.40] tested by the dithizone method GR mixed with 1 part by volume deionised water). Add 5 ml sulfuric acid (about 1.27) (1 part by volume Sulfuric acid 95–97% [about 1.84] GR carefully stirred into 3 parts by volume deionised water), and fume off the nitric acid. Take up the residue in deionised water, transfer to a 1000-ml volumetric flask, and make up to the mark with deionised water. 1 ml ≙ 1 mg Zn^{2+}.

Zinc standard solution: Make the contents of one ampoule of Zinc standard solution Titrisol up to 1000 ml with deionised water. 1 ml ≙ 1 mg Zn^{2+}.

The dilutions necessary for plotting of the reference curve are freshly prepared from the zinc standard solution as required.

Reagents

Cat. No.		Packages
9532	Alkalit® indicator strips pH 7.5–14.0 non-bleeding graduated in 0.5 pH units	1 pack
5432	Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l
1192	Ammonium oxalate GR	250 g, 1 kg
3092	Dithizone (1,5-diphenylthiocarbazone) GR	5 g, 25 g, 100 g
4967	Potassium cyanide GR	100 g, 250 g, 1 kg
6267	Sodium acetate cryst. GR indifferent to potassium permanganate	500 g, 1 kg, 5 kg
6579	di-Sodium hydrogen phosphate 12-hydrate GR	500 g, 1 kg, 5 kg
6498	Sodium hydroxide pellets GR	500 g, 1 kg, 5 kg
6516	Sodium thiosulfate 5-hydrate GR	500 g, 1 kg, 5 kg

9958	Sodium hydroxide solution 0.25 mol/l Titrisol® concentrated solution for preparation of 1 litre of 0.25 N solution	1 amp.
9139	Sodium hydroxide solution 0.25 mol/l	1 l
456	Nitric acid min. 65% (about 1.40) tested by the dithizone method GR	1 l, 2½ l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2½ l
9970	Hydrochloric acid 1 mol/l Titrisol® concentrated solution for preparation of 1 litre of 1 N solution	1 amp.
9057	Hydrochloric acid 1 mol	1 l, 5 l
731	Sulfuric acid 95–97% (about 1.84) GR	1 l, 2½ l
823 310	Hydrogen sulfide	0.44 l
823 311	Hydrogen sulfide	10.0 l
9542	Special indicator strips pH 4.0–7.0 non-bleeding graduated in 0.2–0.3 pH units	1 pack
9543	Special indicator strips pH 6.5–10.0 non-bleeding graduated in 0.2–0.3 pH units	1 pack
2208	Carbon tetrachloride GR (for determinations with dithizone)	1 l, 2½ l
8780	Zinc granular GR	500 g, 1 kg
8883	Zinc sulfate 7-hydrate GR	500 g, 1 kg, 5 kg
9953	Zinc standard solution Titrisol® 1.000 g ± 0.002 g Zn ($ZnCl_4$ in dil. HCl)	1 amp.

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Rapid analysis systems and test kits

Because of their reliability and ease of use, Merck rapid tests enjoy very great popularity. We offer a broad spectrum of instrument based and manual testing possibilities ranging from simple but semi-quantitative test strips right up to quantitative rapid photometric analyses.

The rapid test kits not only permit fast on-site testing but also allow a sort of screening test to be applied in laboratories having a high sample throughput in order to sort out those samples requiring more precise quantitative analysis.

Merckoquant® test strips are suitable for practically all types of water.

Aquamerck® and Aquaquant® test kits are suitable primarily for testing drinking, industrial and boiler-feed water, i.e. water which is generally relatively clean.

Microquant® reagent kits, on the other hand, are intended for testing coloured and slightly turbid water, i.e. their main application is for testing waste water.

Spectroquant® rapid tests are for quick and simple photometric determinations.

Brief description of products

Merckoquant® test strips:

Exploratory tests for rapid preliminary testing of values from 1 mg/l (ppm) upwards.

Aquamerck® test kits:

Simple titrimetric and colorimetric tests for determining numerous water constituents. Titration kits contain dropping bottles, precision droppers or titration pipettes. Colorimetric determinations are performed with colour charts or with Aquamerck® Testing Vessels.

Aquaquant® test kits:

Tube tests in which a sliding colour comparator is used in reflectance mode to provide semi-quantitative results on the presence of important water constituents in the high sensitivity range. Limit values set in drinking water regulations are detected.

Merckoquant® test kits:

Tube tests based on a rotating colour comparator used in transmittance mode to provide semi-quantitative results on important water constituents in the low sensitivity range. Particularly suitable for slightly coloured or turbid water.

Spectroquant® test kits:

Reagent kits for rapid photometric analysis. These are simultaneously the reagent exchange packs used to replenish Microquant®.

Acidity

Method: alkalimetric titration against mixed indicator or phenolphthalein
(determination of −m and −p values)

11108 Aquamerck® **Acidity**
Base consumption or base capacity up to pH 8.2
Reagent kit with graduated titration pipette
(graduations: 0.1 mmol/l)
for 200 determinations

Alkalinity

Method: acidimetric titration against mixed indicator for phenolphthalein
(determination of +m and +p values)

11109 Aquamerck® **Alkalinity**
Acid consumption or acid capacity up to pH 8.2 and pH 4.3
Reagent kit with graduated titration pipette
(graduations: 0.1 mmol/l),
for 200 determinations

Aluminium

Method: colorimetry with aurin tricarboxylic acid

10016 Merckoquant® **Aluminium Test**
Pack containing 100 strips
Colour scale graduations: 0 – 10 – 25 – 50 – 100 – 250 mg/l (ppm)

Ammonium

Method: colorimetry of Nessler's reaction (yellowish-brown colouration)

10024 Merckoquant® **Ammonium Test**
Test strips plus measuring vessel and sodium hydroxide solution
for 50 determinations
Colour scale graduations: 0 – 10 – 30 – 60 – 100 – 200 – 400 mg/l (ppm)

11117	Aquamerck® **Ammonium Test** Reagent kit with colour scale for 150 determinations Colour scale graduations: 0 – 0.5 – 1.0 – 3.0 – 5.0 – 10 mg/l (ppm)
11145	Aquamerck® **Ammonium/Nitrite** Testing Vessel Graduations of the ammonium scale: 0 – 0.5 – 2.0 – 5.0 – 10 mg/l (ppm)
11150	Aquamerck® **Ammonium** Reagent kit for 100 determinations Also required: Testing Vessel 11145
14400	Aquaquant® **Ammonium** Reagent kit with integrated 10-stage colour comparator for 100 determinations Colour scale graduations: 0 – 0.05 – 0.1 – 0.15 – 0.2 – 0.3 – 0.4 – 0.5 – 0.6 – 0.8 mg/l (ppm)
Method:	colorimetry of blue 2,2'-isopropyl-5,5'-methylindophenol (Berthelot's reaction)
14428	Aquaquant® **Ammonium** Reagent kit with integrated 10-stage colour comparator for 60 determinations Colour scale graduations: 0 – 0.025 – 0.05 – 0.075 – 0.1 – 0.15 – 0.2 – 0.25 – 0.3 – 0.4 mg/l (ppm)
14423	Aquaquant® **Ammonium** Reagent kit with integrated 10-stage colour comparator for 250 determinations Colour scale graduations: 0 – 0.2 – 0.5 – 0.8 – 1.2 – 1.6 – 2.0 – 3.0 – 5.0 – 8.0 mg/l (ppm)
14750	Microquant® **Ammonium** Reagent kit with 10-stage rotating comparator for 250 determinations Colour scale graduations: 0 – 0.2 – 0.5 – 0.8 – 1.3 – 2.0 – 3.0 – 4.5 – 6.0 – 8.0 mg/l (ppm)
14752	Spectroquant® **Ammonium** Reagent kit for rapid photometric analysis for 125 to 500 determinations Range: 0.03 – 3.0 mg/l (ppm)

Arsenic

Method: Reduction to hydrogen arsenide, then reaction in the gaseous phase with mercury(II) bromide

10026 Merckoquant® **Arsenic Test**
Test strips, reagents and accessories for 100 determinations
Colour scale graduations: 0 – 0.1 – 0.5 – 1.0 – 1.7 – 3.0 mg/l (ppm)

Calcium

Method: Complexing of calcium ions with glyoxal bis(2-hydroxyanil) in the presence of hydrogen peroxide

10034 Merckoquant® **Calcium Test**
Test strips plus measuring vessel and reagents
for 60 determinations
Colour scale graduations: 0 – 25 – 50 – 100 – 250 mg/l (ppm)

Method: Complexometric titration with Titriplex® III against calcon carboxylic acid

11110 Aquamerck® **Calcium**
Reagent kit with graduated titration pipette
(graduations: 2 mg/l)
for 100 determinations

Chlorine

Method: reaction via cyanogen chloride to glutacondialdehyde and subsequent colorimetry of a polymethine dye

10027 Merckoquant® **Chlorine and Cyanide Test**
Test strips, reagents and accessories
for 100 determinations of each
Chlorine scale graduations: 0 – 4 – 12 – 40 – 120 mg/l (ppm)

Method: colorimetric determination with o-tolidine

11126 Aquamerck® **Chlorine and pH Test**
Reagent kit with colour scale
for 100 determinations of each
Chlorine scale graduations: 0 – 0.2 – 0.4 – 0.6 – 1.0 mg/l (ppm)

11134 Aquamerck® **Chlorine and pH**
Reagent kit with Testing Vessel 8020 Chlorine and pH
for 300 determinations of each
Chlorine scale graduations: 0.1 – 0.3 – 0.6 – 1.0 – 1.5 mg/l (ppm)

Method: colorimetric determination with DPD reagent

11135 Aquamerck® **Chlorine and pH**
Reagent kit with Testing Vessel 11101 Chlorine and pH
for 200 determinations each of free active chlorine, active chlorine and bound active chlorine
Chlorine scale graduations: 0.1 – 0.3 – 0.6 – 1.0 – 1.5 mg/l (ppm)

11120 Aquamerck® **Chlorine and pH**
Reagent kit with Testing Vessel 11101 Chlorine and pH
for 450 determinations each of free active chlorine, active chlorine and bound active chlorine
Chlorine scale graduations: 0.1 – 0.3 – 0.6 – 1.0 – 1.5 mg/l (ppm)

Chloride

Method: mercurimetric titration against diphenylcarbazone

11132 Aquamerck® **Chloride**
Reagent kit with dropping bottle
(graduations: 1 drop = 25 mg/l)
for 50 determinations

11106 Aquamerck® **Chloride**
Reagent kit with graduated titration pipette
(graduations: 2 mg/l)
for 200 determinations

Method: colorimetry of the orange-red iron(III) thiocyanate using the mercury thiocyanate iron(III) procedure

14401 Aquaquant® **Chloride**
Reagent kit with integrated 8-stage colour comparator
for 300 determinations
Colour scale graduations: 0 – 5 – 10 – 20 – 40 – 75 – 150 – 300 mg/l (ppm)

14753 Microquant® **Chloride**
Reagent kit with 10-stage rotating comparator
for 220 determinations
Graduations of the coloured disc: 0 – 3 – 6 – 10 – 18 – 30 – 60 – 100 – 180 – 300 mg/l (ppm)

14755 Spectroquant® **Chloride**
Reagent kit for rapid photometric analysis
for 150–300 determinations
Range: 0.4 – 40 mg/l (ppm)

Chromium

Method: colorimetry of the chromium-diphenylcarbazone complex

10012 Merckoquant® **Chromate Test**
Pack containing 100 strips
Colour scale graduations: 0 – 3 – 10 – 30 mg/l (ppm)

14402 Aquaquant® **Chromium**
Reagent kit with integrated 10-stage colour comparator
for 150 determinations
Colour scale graduations: 0 – 0.005 – 0.01 – 0.02 – 0.03 – 0.04 – 0.05 – 0.06 – 0.08 – 0.1 mg/l (ppm)

14441 Aquaquant® **Chromium**
Reagent kit with integrated 10-stage colour comparator
for 300 determinations
Colour scale graduations: 0 – 0.1 – 0.2 – 0.3 – 0.45 – 0.6 – 0.8 – 1.0 – 1.3 – 1.6 mg/l (ppm)

14756 Microquant® **Chromium**
Reagent kit with 10-stage rotating comparator
for 300 determinations
Graduations of the coloured disc: 0 – 0.1 – 0.2 – 0.35 – 0.6 – 1.0 – 1.8 – 3.0 – 6.0 – 10 mg/l (ppm)

14758 Spectroquant® **Chromium**
Reagent kit for rapid photometric analysis
for 300–600 determinations
Range: 0.025 – 2.5 mg/l (ppm)

Cobalt

Method:	colorimetry with rhodanide ions
10002	Merckoquant® **Cobalt Test** Pack containing 100 strips Colour scale graduations: 0 – 10 – 30 – 100 – 300 – 1000 mg/l (ppm)

Copper

Method:	colorimetry of the blue complex of copper with cuprizon [oxalic acid bis(cyclohexylidene hydrazide)]
10003	Merckoquant® **Copper** Pack containing 100 strips Colour scale graduations: 0 – 10 – 30 – 100 – 300 mg/l (ppm)
14414	Aquaquant® **Copper** Reagent kit with integrated 10-stage colour comparator for 100 determinations Colour scale graduations: 0 – 0.05 – 0.08 – 0.12 – 0.16 – 0.2 – 0.25 – 0.3 – 0.4 – 0.5 mg/l (ppm)
14418	Aquaquant® **Copper** Reagent kit with integrated 10-stage colour comparator for 150 determinations Colour scale graduations: 0 – 0.3 – 0.6 – 1.0 – 1.5 – 2.0 – 2.5 – 3.0 – 4.0 – 5.0 mg/l (ppm)
14765	Microquant® **Copper** Reagent kit with 10-stage rotating comparator for 100 determinations Graduations of the coloured disc: 0 – 0.3 – 0.6 – 1.0 – 1.5 – 2.0 – 3.0 – 5.0 – 7.0 – 10 mg/l (ppm)
14767	Spectroquant® **Copper** Reagent kit for rapid photometric analysis for 200 determinations Range: 0.1 – 9.5 mg/l (ppm)

Cyanide

Method:	colorimetry of the violet reaction product from cyanogen chloride, pyridine and N,N'-dimethylbarbituric acid
10027	Merckoquant® **Chlorine and Cyanide Test** Test strips, reagents and accessories for 100 determinations of each Cyanide scale graduations: 0 – 1 – 3 – 10 – 30 mg/l (ppm)
14417	Aquaquant® **Cyanide** Reagent kit with integrated 10-stage colour comparator for 65 determinations Colour scale graduations: 0 – 0.002 – 0.004 – 0.007 – 0.01 – 0.013 – 0.016 – 0.02 – 0.025 – 0.03 mg/l (ppm)
14429	Aquaquant® **Cyanide** Reagent kit with integrated 10-stage colour comparator for 200 determinations Colour scale graduations: 0 – 0.03 – 0.06 – 0.1 – 0.15 – 0.2 – 0.3 – 0.4 – 0.5 – 0.7 mg/l (ppm)
14798	Microquant® **Cyanide** Reagent kit with 10-stage rotating comparator for 200 determinations Graduations of the coloured disc: 0 – 0.03 – 0.07 – 0.13 – 0.2 – 0.3 – 0.5 – 1.0 – 2.0 – 5.0 mg/l (ppm)
14800	Spectroquant® **Cyanide** Reagent kit for rapid photometric analysis for 130–400 determinations Range: 0.005 – 0.5 mg/l (ppm)

Hardness

Carbonate hardness (ABC)

Method:	acidimetric titration against mixed indicator
11103	Aquamerck® **Carbonate Hardness Test** Reagent kit with dropping bottle (graduations: 1 drop = 1°d) for 50 determinations at 10°d

8048 Aquamerck® **Carbonate Hardness**
Acid binding capacity (ABC) or acid capacity up to pH 4.3
Reagent kit with graduated titration pipette
(graduations: 0.2 meq/l and 0.2°d)
for 400 determinations at 10°d

11147 Aquamerck® **ABC Test**
+m value, acid capacity up to pH 4.3
for 100 determinations at ABC = 2.5 mmol/l
Graduations: 1 drop = 0.25 mmol/l

Total hardness (sum of alkaline earths)

Method: complexing reaction with Titriplex® III

10025 Merckoquant® **Total Hardness Test (sum of alkaline earths)**
Pack containing 100 strips
Test strips for determining water hardness. Range: 3–23°d

Method: complexometric titration with Titriplex® III against mixed indicator tablet

8011 Aquamerck® **Total Hardness (sum of alkaline earths)**
Reagent kit with precision dropper
(graduations: 1 drop = 1°d)
for 100 determinations at 10°d

Method: complexometric titration with Titriplex® III against mixed indicator (indicator solution)

11104 Aquamerck® **Total Hardness Test (sum of alkaline earths)**
Reagent kit with dropping bottle
(graduations: 1 drop = 1°d)
for 50 determinations at 10°d

11111 Aquamerck® **Total Hardness (sum of alkaline earths)**
Reagent kit with precision dropper
(graduations: 1 drop = 1°d)
for 100 determinations at 10°d

8039 Aquamerck® **Total Hardness (sum of alkaline earths)**
Reagent kit with graduated titration pipette
(graduations: 0.2 meq/l and 0.2°d)
for 400 determinations at 10°d

8047 Aquamerck® **Total Hardness (sum of alkaline earths)**
Reagent kit with graduated titration pipette
(graduations: 1 ppm $CaCO_3$ and 0.25°d)
for 200 determinations (at 3°d) in water of low hardness

Permanent hardness

Method: Colour reaction with Eriochrome black T – mixed indicator solution

11142 Aquamerck® **Permanent Hardness Test**
Reagent kit for 300 determinations

Hydrazine

Method: colorimetry with 4-dimethylaminobenzaldehyde

8018 Aquamerck® **Hydrazine Testing Vessel**
Colour scale graduations: 0 – 0.1 – 0.25 – 0.5 – 1.0 mg/l (ppm)

8017 Aquamerck® **Hydrazine**
Reagent solution for 100 determinations

11139 Aquamerck® **Hydrazine**
Reagent solution for 200 determinations

Method: reaction with Zinospectral to give red 4-(dimethylamino)cinnamaldehyde azine

14427 Aquaquant® **Hydrazine**
Reagent kit with integrated 8-stage colour comparator
for 125 determinations
Colour scale graduations: 0 – 0.02 – 0.04 – 0.07 – 0.1 – 0.14 – 0.18 – 0.25 mg/l (ppm)

14405 Aquaquant® **Hydrazine**
Reagent kit with integrated 10-stage colour comparator
for 250 determinations
Colour scale graduations: 0 – 0.2 – 0.4 – 0.6 – 0.8 – 1.0 – 1.5 – 2.0 – 3.0 – 4.0 mg/l (ppm)

14795 Microquant® **Hydrazine**
Reagent kit with integrated 10-stage rotating comparator
for 250 determinations
Colour scale graduations: 0 – 0.2 – 0.4 – 0.6 – 0.8 – 1.0 – 1.5 – 2.0 – 3.0 – 4.0 mg/l (ppm)

14797 Spectroquant® **Hydrazine**
Reagent kit for rapid photometric analysis
for 250–500 determinations
Range: 0.05 – 4.5 mg/l (ppm)

Hydrogen sulfide

Method: colorimetry of methylene blue

14416 Aquaquant® **Hydrogen Sulfide**
Reagent kit with integrated 10-stage colour comparator
for 100 determinations
Colour scale graduations: 0 – 0.02 – 0.04 – 0.06 – 0.08 – 0.1 – 0.13 – 0.16 – 0.2 – 0.25 mg/l (ppm)

14435 Aquaquant® **Hydrogen Sulfide**
Reagent kit with integrated 10-stage colour comparator
for 200 determinations
Colour scale graduations: 0 – 0.2 – 0.4 – 0.7 – 1.0 – 1.5 – 2.0 – 2.5 – 3.5 – 5.0 mg/l (ppm)

14777 Microquant® **Hydrogen Sulfide**
Reagent kit with integrated 10-stage colour comparator
for 200 determinations
Graduations of the coloured disc: 0 – 0.1 – 0.3 – 0.5 – 0.7 – 1.0 – 2.0 – 3.0 – 4.0 – 5.0 mg/l (ppm)

14779 Spectroquant® **Hydrogen Sulfide**
Reagent kit for rapid photometric analysis
for 200–400 determinations
Range: 0.03 – 3.3 mg/l (ppm)

Iron

Method:	colorimetric determination with 2,2'-bipyridine
10004	Merckoquant® **Iron Test** Pack containing 100 strips Colour scale graduations: 0 – 3 – 10 – 25 – 50 – 100 – 250 – 500 mg/l (ppm)
11136	Aquamerck® **Iron** Reagent kit with Testing Vessel 8013 for 180 determinations (Fe^{2+}/Fe^{3+}) Colour scale graduations: 0.1 – 0.3 – 0.5 – 1.0 – 2.5 – 5.0 – 7.5 – 12.5 – 25 – 50 mg/l (ppm)
Method:	colorimetry of the red-orange complex of iron with 1,10-phenanthroline
14404	Aquaquant® **Iron** Reagent kit with integrated 10-stage colour comparator for 500 determinations Colour scale graduations: 0 – 0.25 – 0.5 – 1.0 – 2.0 – 3.0 – 5.0 – 7.5 – 10.0 – 15.0 mg/l (ppm)
Method:	colorimetry of the red-violet complex of iron with Ferrospectral [3-(2-pyridyl)-5,6-bis(5-phenylsulfonic acid)-1,2,4-triazine disodium salt]
14403	Aquaquant® **Iron** Reagent kit with integrated 10-stage colour comparator for 300 determinations Colour scale graduations: 0 – 0.01 – 0.02 – 0.03 – 0.04 – 0.06 – 0.08 – 0.1 – 0.15 – 0.2 mg/l (ppm)
14438	Aquaquant® **Iron** Reagent kit with integrated 10-stage colour comparator for 500 determinations Colour scale graduations: 0 – 0.2 – 0.4 – 0.6 – 0.8 – 1.0 – 1.3 – 1.6 – 2.0 – 2.5 mg/l (ppm)
14759	Microquant® **Iron** Reagent kit with 10-stage rotating comparator for 500 determinations Graduations of the coloured disc: 0 – 0.1 – 0.2 – 0.3 – 0.5 – 0.8 – 1.2 – 2.0 – 3.0 – 5.0 mg/l (ppm)

14761 Spectroquant® **Iron**
Reagent kit for rapid photometric analysis
for 600–1000 determinations
Range: 0.04 – 4.0 mg/l (ppm)

Magnesium

Method: colorimetry with Mann and Yoe reagent yielding a red dye

11131 Aquamerck® **Magnesium**
Reagents and accessories for 50 determinations
Colour scale graduations: 0 – 100 – 200 – 300 – 500 – 1000 – 1500 mg/l (ppm)

Manganese

Method: redox reaction between manganese dioxide and o-tolidine

10005 Merckoquant® **Manganese Test**
Pack containing 100 strips
Colour scale graduations: 0 – 5 – 25 – 100 – 500 mg/l (ppm)

Method: colorimetry of the red-brown colour complex of manganese with formaldoxime

14406 Aquaquant® **Manganese**
Reagent kit with integrated 10-stage colour comparator
for 110 determinations
Colour scale graduations: 0 – 0.03 – 0.06 – 0.1 – 0.15 – 0.2 – 0.25 – 0.3 – 0.4 – 0.5 mg/l (ppm)

14768 Microquant® **Manganese**
Reagent kit with 10-stage rotating comparator
for 110 determinations
Graduations of the coloured disc: 0 – 0.3 – 0.7 – 1.3 – 2.0 – 3.0 – 4.0 – 5.0 – 7.0 – 10 mg/l (ppm)

14770 Spectroquant® **Manganese**
Reagent kit for rapid photometric analysis
for 220 determinations
Range: 0.12 – 12 mg/l (ppm)

Nickel

Method:	reaction with diacetyldioxime to yield a red complex
10006	Merckoquant® **Nickel Test** Pack containing 100 strips Colour scale graduations: 0 – 10 – 25 – 100 – 250 – 500 mg/l (ppm)
14420	Aquaquant® **Nickel** Reagent kit with integrated 10-stage colour comparator for 250 determinations Colour scale graduations: 0 – 0.25 – 0.5 – 0.75 – 1.0 – 1.5 – 2.0 – 3.0 – 4.0 – 5.0 mg/l (ppm)
14783	Microquant® **Nickel** Reagent kit with 10-stage rotating comparator for 500 determinations Colour scale graduations: 0 – 0.5 – 1.0 – 1.5 – 2.0 – 3.0 – 4.0 – 6.0 – 8.0 – 10 mg/l (ppm)
14785	Spectroquant® **Nickel** Reagent kit for rapid photometric analysis for 250–1000 determinations Range: 0.1 – 10 mg/l (ppm)

Nitrate

Method:	reduction to nitrite, diazotisation and coupling to yield a red-violet dye
10020	Merckoquant® **Nitrate Test** Pack containing 50 strips Colour scale graduations: 0 – 10 – 30 – 100 – 250 – 500 mg/l (ppm)

Nitrite

Method:	colorimetric determinations with sulfanilic acid and N-(1-naphthyl)-ethylenediammonium dichloride
10007	Merckoquant® **Nitrite Test** Pack containing 100 strips Colour scale graduations: 0 – 1 – 5 – 10 – 25 – 50 mg/l (ppm)

Brief description of products

11118	Aquamerck® **Nitrite Test** Reagent kit with colour scale for 150 determinations Colour scale graduations: 0 – 0.05 – 0.1 – 0.25 – 0.5 – 1.0 mg/l (ppm)
8037	Aquamerck® **Nitrite Testing Vessel** Colour scale graduations: 0.025 – 0.05 – 0.1 – 0.25 – 0.5 – 1.0 – 2.0 – 5.0 – 10.0 – 20.0 mg/l (ppm)
8036	Aquamerck® **Nitrite** Reagent kit for 50 determinations Also required: Testing Vessel 8037
11128	Aquamerck® **Nitrite** Reagent kit for 100 determinations Also required: Testing Vessel 8037
14408	Aquaquant® **Nitrite** Reagent kit with integrated 10-stage colour comparator for 110 determinations Colour scale graduations: 0 – 0.005 – 0.012 – 0.02 – 0.03 – 0.04 – 0.05 – 0.06 – 0.08 – 0.1 mg/l (ppm)
14424	Aquaquant® **Nitrite** Reagent kit with integrated 10-stage colour comparator for 400 determinations Colour scale graduations: 0 – 0.1 – 0.2 – 0.3 – 0.4 – 0.6 – 0.8 – 1.0 – 1.3 – 2.0 mg/l (ppm)
14774	Microquant® **Nitrite** Reagent kit with 10-stage rotating comparator for 400 determinations Graduations of the coloured disc: 0 – 0.1 – 0.2 – 0.4 – 0.6 – 1.0 – 1.8 – 3.0 – 6.0 – 10 mg/l (ppm)
14776	Spectroquant® **Nitrite** Reagent kit for rapid photometric analysis for 220–800 determinations Range: 0.03 – 3.0 mg/l (ppm)

Oxygen

Method:	Winkler titration
11107	Aquamerck® **Oxygen** Reagent kit with graduated titration pipette Graduations: 0.1 mg/l for 100 determinations at 8.5 mg/l O_2
11149	Aquamerck® **Oxygen, Oxygen Requirement (BOD)** Compact Laboratory with graduated titration pipette (graduations: 0.1 mg/l), 3 oxygen bottles, 50-ml syringe for withdrawing sample, thermometer and glass beads for 300 determinations at 8.5 mg/l O_2

pH

Method:	colorimetric determination with mixed indicator
11137	Aquamerck® **pH Test** Reagent kit with colour scale pH 4.5 – 9.0 (graduations: 0.5 pH units) for 100 determinations
8038	Aquamerck® **pH** Reagent kit with Testing Vessel pH 4.5 – 9.0 (graduations: 0.5 pH units) for 100 determinations
9177	**Indicator solution** Reagent solution with colour scale pH 0 – 5 Graduations: 0.5 pH units 100 ml
9176	**Indicator solution** Reagent solution with colour scale pH 9 – 13 Graduations: whole pH units 100 ml
9175	**Universal indicator solution** Reagent solution with colour scale pH 4 – 10 Graduations: 0.5 pH units 100 ml

Further pH determinations can be performed with non-bleeding pH indicator strips. For a list of these please see page 158.

Phosphate

Method:	colorimetric determination with ammonium heptamolybdate
11138	Aquamerck® **Phosphate** Reagent kit with Testing Vessel 8014 Phosphate/Silicate for 150 determinations Graduations of the phosphate scale: 1 – 2.5 – 5 – 7.5 – 10 mg/l (ppm) P_2O_5
Method:	colorimetric determination with vanadate/molybdate
8015	Aquamerck® **Phosphate Testing Vessel** Colour scale graduations: 2.4 – 8.6 – 13 – 24 – 32 mg/l (ppm) P_2O_5
11125	Aquamerck® **Phosphate** Reagent kit for 850 determinations Also required: Testing Vessel 8015
8498	Vanadate/molybdate reagent 500 ml of reagent solution Also required: Testing Vessel 8015

Phosphorus

Method:	colorimetric determination with α-phosphomolybdic acid (α-phosphomolybdenum blue)
14409	Aquaquant® **Phosphorus** Reagent kit with integrated 10-stage colour comparator for 200 determinations Colour scale graduations: 0 – 0.01 – 0.02 – 0.03 – 0.045 – 0.06 – 0.08 – 0.1 – 0.13 – 0.16 mg/l (ppm)
14431	Aquaquant® **Phosphorus** Reagent kit with integrated 10-stage colour comparator for 300 determinations Colour scale graduations: 0 – 0.1 – 0.2 – 0.35 – 0.5 – 0.7 – 1.0 – 1.5 – 2.0 – 2.5 mg/l (ppm)

14786 Microquant® **Phosphorus**
Reagent kit with 10-stage rotating comparator
for 600 determinations
Graduations of the coloured disc: 0 – 0.1 – 0.2 – 0.35 – 0.5 – 0.7 – 1.0 – 1.5 – 2.0 – 3.0 mg/l (ppm)

14788 Spectroquant® **Phosphorus**
Reagent kit for rapid photometric analysis
for 300–1200 determinations
Range: 0.024–2.4 mg/l (ppm)

Phosphate/Silicate

Method: colorimetric determinations with ammonium heptamolybdate

11119 Aquamerck® **Phosphate/Silicate**
Reagent kit with Testing Vessel 8014 Phosphate/Silicate
for 180 determinations
Graduations of the phosphate scale: 1 – 2.5 – 5 – 7.5 – 10 mg/l (ppm) P_2O_5
Graduations of the silicate scale: 0.3 – 0.7 – 1.5 – 2.2 – 3.0 mg/l (ppm) SiO_2

Potassium

Method: colorimetry with dipicrylamine

10018 Merckoquant® **Potassium Test**
Pack containing 100 strips
Colour scale graduations: 0 – 300 – 700 – 1000 – 2000 mg/l (ppm)

Silicon

Method: colorimetry of reduced ß-silicomolybdic acid (ß-silicomolybdenum blue)

14410 Aquaquant® **Silicon**
Reagent kit with integrated 10-stage colour comparator
for 150 determinations
Colour scale graduations: 0 – 0.01 – 0.02 – 0.04 – 0.06 – 0.08 – 0.1 – 0.15 – 0.2 – 0.25 mg/l (ppm)

14433 Aquaquant® **Silicon**
Reagent kit with integrated 10-stage colour comparator
for 150 determinations
Colour scale graduations: 0 – 0.2 – 0.4 – 0.7 – 1.0 – 1.5 – 2.0 – 2.5 – 3.0 – 4.0 mg/l (ppm)

14792 Microquant® **Silicon**
Reagent kit with 10-stage rotating comparator
for 150 determinations
Graduations of the coloured disc: 0 – 0.3 – 0.6 – 1.0 – 1.5 – 2.0 – 3.0 – 5.0 – 7.0 – 10 mg/l (ppm)

14794 Spectroquant® **Silicon**
Reagent kit for rapid photometric analysis
for 300 determinations
Range: 0.03 – 8.0 mg/l (ppm)

Silver

Method: reaction with cadmium sulfide

10008 Merckoquant® **Fixing Bath Test**
Pack containing 100 strips
Colour scale graduations: 0 – 0.5 – 1 – 1.7 – 3 – 5 – 7 – 10 g/l silver

Sulfate

Method: colorimetry of red thorin-barium complex

10019 Merckoquant® **Sulfate Test**
Pack containing 100 strips
Range: 200 – 900 mg/l (ppm)

Sulfide

see Hydrogen sulfide

Sulfite

Method: reaction with sodium nitroprusside, potassium hexacyanoferrate(II) and zinc sulfate to yield a colour complex

10013 Merckoquant® **Sulfite Test**
Pack containing 100 strips
Colour scale graduations: 0 – 10 – 40 – 125 – 500 mg/l (ppm)

Tin

Method: colorimetric determination with toluene-3,4-dithiol

10028 Merckoquant® **Tin Test**
Test strips and reagent
for 50 determinations
Colour scale graduations: 0 – 10 – 25 – 50 – 100 – 200 mg/l (ppm)

Water, intrinsic colour

Method: optical/visual colorimetry of yellowish intrinsic colour against simulated platinum-cobalt standard according to Hazen

14421 Aquaquant® **Color**
Test kit with integrated 10-stage colour comparator
Colour scale graduations: 0 – 5 – 10 – 20 – 30 – 40 – 50 – 70 – 100 – 150 Hazen

Zinc

Method: colorimetric determination with dithizone

10038 Merckoquant® **Zinc Test**
Test strips plus measuring vessel and reagent
for 100 determinations
Colour scale graduations: 0 – 10 – 40 – 100 – 250 mg/l (ppm)

Method: colorimetry of the blue-green complex of zinc with thiocyanate and brilliant green in an acid medium

14412 Aquaquant® **Zinc**
Reagent kit with integrated 10-stage colour comparator
for 150 determinations
Colour scale graduations: 0 – 0.1 – 0.2 – 0.3 – 0.4 – 0.5 – 0.7 – 1.0 – 2.0 – 5.0 mg/l (ppm)

14780 Microquant® **Zinc**
Reagent kit with 10-stage rotating comparator
for 120 determinations
Graduations of the coloured disc: 0 – 0.1 – 0.2 – 0.3 – 0.4 – 0.5 – 0.7 – 1.0 – 2.0 – 5.0 mg/l (ppm)

Water laboratories

11151 Aquamerck® **Water Laboratory for Open Stretches of Water**
Reagent kit for determining ammonium, carbonate hardness (ABC), nitrite, pH and oxygen

11102 Aquamerck® **Water Laboratory for Aquaristics and Fish Farming**
Reagent kit for determining total hardness, carbonate hardness, pH, ammonium, nitrite and nitrate

11112 Aquamerck® **Water Laboratory for the Building Industry**
For testing for water aggressive to concrete
Reagent kit for determining ammonium, carbonate hardness, chloride, total hardness, odour (H_2S), lime-dissolving CO_2, magnesium, pH and sulfate

11146 Aquamerck® **Ammonium, Nitrite and pH**
Reagent kit for determining ammonium, nitrite and pH

The Testing of Water

MERCK

E. Merck, Darmstadt
Federal Republic of Germany

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