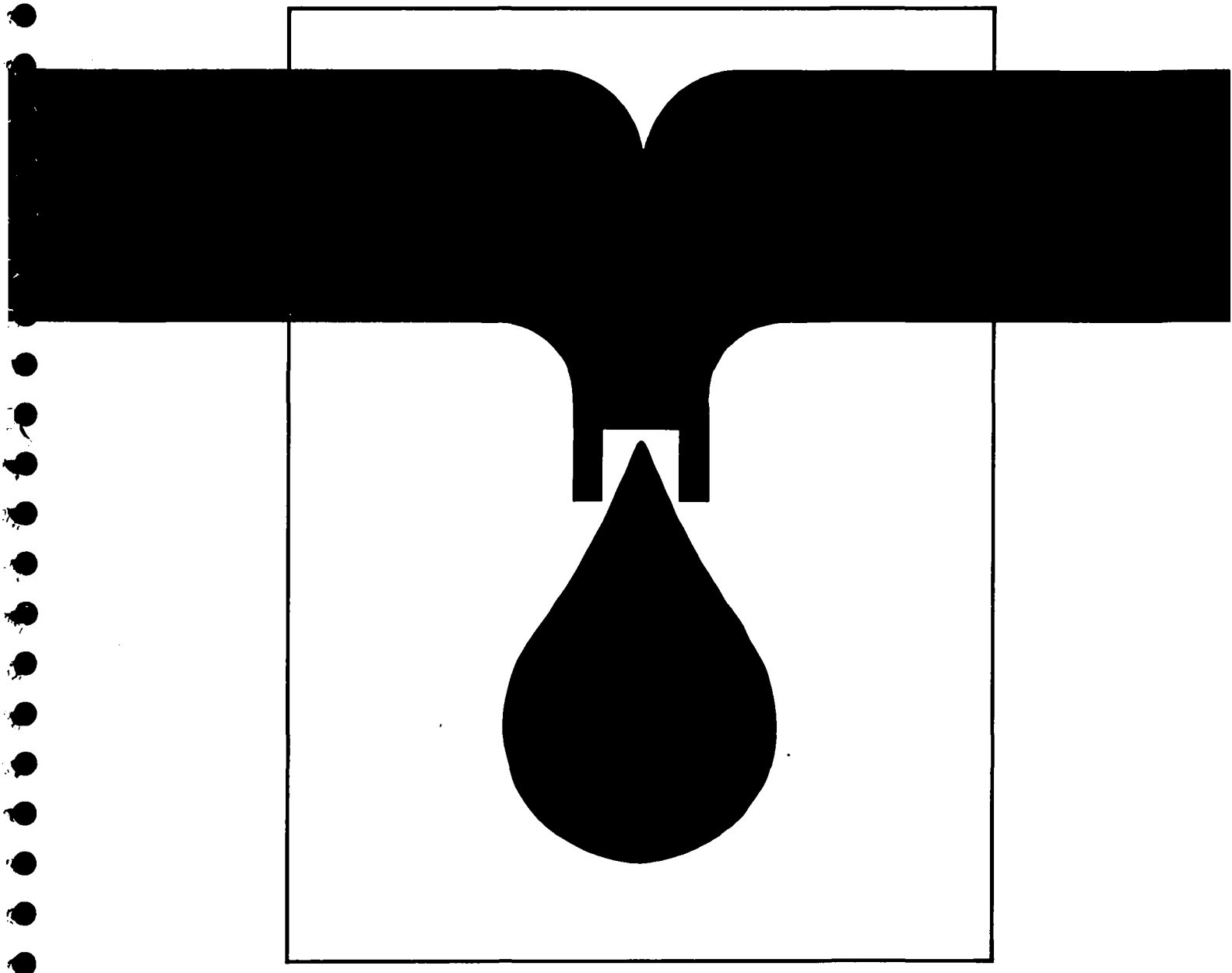
TRAINING MODULES
FOR
WATERWORKS PERSONNEL



Special Skills

3.2

Performance of simple water analysis

Foreword

Even the greatest optimists are no longer sure that the goals of the UN "International Drinking Water Supply and Sanitation Decade", set in 1977 in Mar del Plata, can be achieved by 1990. High population growth in the Third World combined with stagnating financial and personnel resources have led to modifications to the strategies in cooperation with developing countries. A reorientation process has commenced which can be characterized by the following catchwords:

- use of appropriate, simple and – if possible – low-cost technologies,
- lowering of excessively high water-supply and disposal standards,
- priority to optimal operation and maintenance, rather than new investments,
- emphasis on institution-building and human resources development.

Our training modules are an effort to translate the last two strategies into practice. Experience has shown that a standardized training system for waterworks personnel in developing countries does not meet our partners' varying individual needs. But to prepare specific documents for each new project or compile them anew from existing materials on hand cannot be justified from the economic viewpoint. We have therefore opted for a flexible system of training modules which can be combined to suit the situation and needs of the target group in each case, and thus put existing personnel in a position to optimally maintain and operate the plant.

The modules will primarily be used as guidelines and basic training aids by GTZ staff and GTZ consultants in institution-building and operation and maintenance projects. In the medium term, however, they could be used by local instructors, trainers, plant managers and operating personnel in their daily work, as check lists and working instructions.

45 modules are presently available, each covering subject-specific knowledge and skills required in individual areas of waterworks operations, preventive maintenance and repair. Different combinations of modules will be required for classroom work, exercises, and practical application, to suit in each case the type of project, size of plant and the previous qualifications and practical experience of potential users.

Practical day-to-day use will of course generate hints on how to supplement or modify the texts. In other words: this edition is by no means a finalized version. We hope to receive your critical comments on the modules so that they can be optimized over the course of time.

Our grateful thanks are due to

Prof. Dr.-Ing. H.P. Haug
and
Ing.-Grad. H. Hack

for their committed coordination work and also to the following co-authors for preparing the modules:

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It is my sincere wish that these training modules will be put to successful use and will thus support world-wide efforts in improving water supply and raising living standards.

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Eschborn, May 1987

Title: Performance of simple water analyses

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0. Introduction:

Methods which can be used in the performance of simple water analyses are regarded here as being those procedures which can be carried out on the spot and in simply equipped water laboratories.

The methods which require a well-equipped water laboratory and appropriately trained personnel will not be discussed. If such methods are required, the GTZ's collection of water analysis methods should be consulted.

A recommended overview of simple methods for microbiological and physico-chemical/chemical water analysis is to be found in the book by L.G. Hutton listed under "Aids". Also to be recommended, however, are the well-formulated information publications by the companies which manufacture reagents and equipment for simple water analyses. The following companies and their publications were consulted in the compilation of this module:

Merck, D-6100 Darmstadt, FRG:
Aquamerck, reagent sets for water analysis
Aquaquant, water analysis system
Macherey-Nagel & Co., D-5160 Düren, FRG:
Test kits for the analysis of drinking water/industrial water/bathing water and waste water using the principles of visual colorimetry
Nanocolor, the analysis system in a portable, compact design
Indicator and test papers, test kits for water analysis
VDSF water analysis systems, D-6050 Offenbach, FRG
Hach Company, Loveland, Colorado, USA
German agents: Struers, D-4000 Düsseldorf, FRG:
Products for water analysis
Water handbook (German and English)
Devices and apparatus for the monitoring and analysis of water and waste water
Miniature colorimeter with direct indicator
Hölzle und Chelius, D-6000 Frankfurt am Main, FRG (agents for the Hellige company)
Sartorius GmbH, D-3400 Göttingen, FRG;
Sartorius membrane filters
(Company publications on microbiological water analysis)
Millipore, Millipore GmbH, D-6078 Neu-Isenburg, FRG:
Information on microbiological water analysis using the membrane filter method and the Millipore sampler

Dr. B. Lange, D-4000 Düsseldorf 11, FRG:
Water analysis handbook
The cuvette test system
Hellige, manufacturers of scientific apparatus, D-7800 Freiburg, FRG

The order in which these companies are listed does not represent an order of merit.

Provided that the manufacturer's instructions are observed in each case, the water testing systems offered by the companies listed above permit water analyses which, although simple, certainly produce usable results which in many cases are in no way inferior to those obtained during a laboratory analysis using more complicated methods. If simple water analyses are to be performed, it is advisable to obtain ready-for-use test systems, since these make it possible for a less skilled member of personnel or a non-specialist to obtain useful results. In the case of somewhat more complex analyses, preference should be given to the colorimetric, photometric, titrimetric and electrometric methods. Even the use of test rods or test papers and simple colour comparisons, however, can also produce usable information, e.g. when measuring the pH value or when testing for nitrates etc.

If these ready-for-use reagents are employed, irrespective of whether they are in rod or paper form, or consist of liquids, solids or tablets, the specified storage life must be observed and secondary reactions, e.g. with the atmospheric oxygen, excluded in accordance with the instructions for use supplied by the individual companies. A functional check should always be performed. Experience has shown for example, that the reagents for measuring active chlorine may for some reason or other become unusable and yield no reaction, even though the odour suggests that the water contains sizeable quantities of chlorine. The same applies to cases in which the water has a clearly acidic taste and the pH value measured is in the neutral or slightly alkaline range. In such cases the measurements are to be repeated using new, fresh reagents. In addition to precise adherence to the manufacturer's instructions, therefore, a critical attitude is required even when using these simple water analysis systems.

1. Principles for simple physico-chemical and chemical water analyses

1.1 Test rods and test papers

The most common area of use for such systems is the measurement of the pH value. Specific colour indicators located on the inner wall of a test rod or on the test papers, in some cases with a variety of zones, change colour according to the pH value of the water under investigation. The colour change is then compared with a colour comparison scale.

Other test rods for use in water analysis have a reaction zone on a piece of plastic sheet, which is inactive when dry and which, for the purpose of the analysis, is immersed in the water under investigation. Once the specified contact time has elapsed, the changed colours are compared with the reference colours and classified in the scale. Using this method, it is possible to determine roughly the water constituents in question.

For the scope of analysis described here, test rods and test papers are available for pH value, ammonium, nitrite, nitrate, sulphate and iron, as well as - for example - aluminium, if, for instance, the functioning of flocculation plants used in water treatment is to be checked. Also commercially available are test rods with which the water hardness can be estimated, for example, in graduations of 5° dH (German degrees of hardness). There are likewise suitable test papers for establishing quickly whether free chlorine is present and in what concentration ranges. As can be seen, even the very simple use of test rods or papers on the spot can in itself yield initial information on water quality. When using such systems it must of course always be borne in mind that the results should be regarded only as representing orders of magnitude; they are, however, extremely useful in this respect.

1.2 Colorimetric methods

The principle behind colorimetric methods is based on the fact that with the aid of a suitable reagent, a coloured compound is formed with the water constituent to be determined, with the depth of the colour of this compound, in a specific range, being proportional to the concentration of the parameter to be determined. In other words, conclusions can be drawn as regards to the concentration of the substance in question on the basis of the depth of the colour of the reaction product.

1.2.1 Visual colour comparison methods

Test rods and test papers to a certain extent themselves represent colorimetric methods (1.1). A greater detection sensitivity and improved estimation of concentrations can be obtained, however, if the colour reactions are carried out in the water sample itself, i.e. not on the relatively small surface of the test rod or paper, and the colour intensities are then compared, e.g. with standard solutions. The reaction colour can then be readily classified among the graduated reference colours in a very simple way. These reactions can be carried out in test tubes or in beakers, graduated cylinders etc. Simple colorimetric determination is also possible, however, using so-called Nessler cylinders; in this method, one of the two coloured liquids is drained off by means of a cock at the bottom until the liquids, when looked through, are seen to be of an identical colour.

It should be pointed out that these simple colorimetric methods - given appropriate experience and skilful use - can certainly yield useful analysis results, paricularly if the water samples to be investigated are coloured or turbid. The human eye can distinguish better between the reaction colour and the fundamental colour or turbidity than an electrical measuring system can.

A number of the analysis systems available from the companies listed are based on this direct visual comparison of coloured water samples.

Mention should also be made in this connection of the so-called "cuvette tests". Here, the colour reaction is carried out in the cuvette itself and the resultant depth of colour, which in a specific range is proportional to the concentration of the constituent in question, evaluated using a colour comparison scale.

This test system has in part also been developed to the point where the depth of colour produced is evaluated using photometric methods.

1.2.2 Simple comparators for use in water analysis

Here again, a colour reaction is carried out in the water under investigation and the colour comparison made against transparent coloured glass or coloured plastics. As a rule, evaluation takes the form of holding the comparator against the light at eye level and classifying the colour of the analysis solution among the reference colours. Compensation can

be made for turbid or coloured initial solutions by measuring this water sample in a reference cuvette against the water sample in which the colour reaction was carried out.

1.2.3 Rotary comparators or similar systems

Here, the reference colours for the individual determinations are in each case on a rotating disc, so that it is relatively easy to assign the depth of colour of the analysis solution to a colour range and thus to a concentration. A separate colour disc is required for every water constituent to be determined using this method. The natural colour of the water under analysis is compensated for by means of a second cuvette. In addition to colour discs with graduated colour changes, discs with a continuous colour scale are also available. Use of such a device involves moving two circular plastic elements running in opposite directions; this permits both a more detailed graduation of the concentration and a larger measuring range.

By using colour surfaces with larger layers, as well as colour surfaces with correspondingly fine graduations (colour scale sliding comparator), sensitivity can be increased such that many concentration ranges which are of importance in drinking-water analysis can be covered.

1.3 Photometric methods

Section 1.2 above discussed all the methods in which the colour comparison for determining the concentration of a specific water constituent is performed visually. The result is thus always determined in part by the capacity of the human eye. This may be an advantage if slight colouring not caused by the reaction or turbidity is to be eliminated in the colour comparison. However, it is difficult for the naked eye to recognize slight differences in colour and the sensitivity of visual colour comparison measurement is also limited. In the photometric methods described briefly below, a specific constituent to be determined in quantitative terms is likewise made to form a coloured compound by means of a chemical reaction. The solution is then irradiated with light of a specific wavelength; the light is absorbed according to the colour intensity. The intensity of the light with which the solution is irradiated (I_0) is reduced as it passes through the sample solution and the residual intensity (I) is measured on the other side, with a photocell, for example, being used as a detector. Every coloured compound has a more or less marked

absorption maximum and the aim is to measure in this maximum, i.e. the wavelength of the light used for irradiation should be as close as possible to this maximum. In the simple water analysis under discussion here the measurements are generally made within the visible range, roughly between 400 and 800 nm. The almost monochromatic light can be isolated from a polychromatic light beam by means of a discrete filter, a graduated filter, a prism or a grating. Metal vapour lamps such as mercury or cadmium vapour lamps emit light of specific different wavelengths. If a filter which is permeable for the required wavelength is placed between the metal vapour lamp and the test solution, monochromatic light for the measurement is likewise obtained.

Both filter photometers, which separate out individual wavelength ranges from a light continuum, and spectrophotometers or photometers with metal vapour lamps are suitable for the simple water analyses under discussion here (the GTZ's collection of water analysis methods should be consulted for the purpose of further introduction to the theory of photometric methods for content determination in water analysis).

The attenuation of the light after it has passed through the coloured solution is a measure of the concentration of the substance in question and can be used for the purpose of content determination with the aid of a reference solution of a known concentration or a calibration curve or calibration constant. The photometers used today for simple water analysis in the field incorporate such calibration and give the results - employing alternating scales - directly as a concentration in, for example, mg/l. These systems can also be used without problems by a non-specialist, since all the reagents are supplied in portion-sized packs. If the detailed instructions for use provided with the equipment are observed, flawless results can be expected.

1.4 Titrimetic methods

Such methods are also known as volumetric analysis. The basic principle involves adding an indicator to a water sample (pretreated if necessary) and then mixing the analysis solution with a volumetric solution until, for example, a colour change takes place or the end point of the titration is recognized, e.g. electrometrically. The titration can be performed using the burettes commonly employed in the past. For the purpose of simple water analysis under field conditions today, however,

it is carried out using titration pipettes, special titrator systems or the drop count method. Even this last-mentioned extremely simple method, which involves counting the drops added and converting the figure to the concentration as specified in the instructions for use, can produce entirely usable results, e.g. when determining the so-called total hardnesses, as well as for the p-value, m-value and carbon dioxide.

The methods which employ titration pipettes (Merck) or digital titrators (Hach) have also proved particularly successful.

1.5 Electrometric methods

Electrometric methods for simple water analysis which have proved particularly successful are those used for measuring the pH value, electrical conductivity, redox potential and oxygen content. The GTZ's collection of water analysis methods should be consulted as regards the theoretical fundamentals. In principle, these methods involve measuring a potential difference between a measuring electrode and a reference electrode. For the purpose of the measurements listed above, simple measuring apparatus (with instructions for use) is available on the market today which is not only inexpensive but also permits a layman to perform the relevant measurements. The measuring devices are available in the form of mains-operated devices, combined mains/storage battery devices and battery-operated devices; only the last two types are suitable for use in the field.

If a single-rod measuring chain is used, measurement of the pH value requires nothing more than immersion of the chain and reading of the value once it has stabilized. It is advisable to calibrate the apparatus using suitable buffer solutions with a known pH value and to check the gradient of the measured values by using three different buffer solutions.

For measurement of electrical conductivity, use is made of the fact that the substances dissolved in the water dissociate, to a greater or lesser extent, into ions. In an electric field, the anions gravitate towards the positively charged anode and the cations toward the negatively charged cathode. Given a comparable constant temperature, the measured electrical conductivity of a water is roughly a function of its ion concentration and thus of its dissolved conductive constituents. Conclusions can therefore be drawn from the measured electrical conductivity as regards the quantity of the dissolved consituents in the water, i.e. its salt or mineral content. The results of electrical conductivity measurements are

highly dependent on temperature, which means either that a specific temperature must always be set before the measurement or that the measurement temperature must be specified. It is also possible to convert the conductivity measured at one temperature to another temperature with the aid of suitable tables (see the GTZ's collection of water analysis methods). Conductivity measurements can be checked using calibration solutions with a known salt content, e.g. with a known sodium chloride or potassium chloride content etc.

Measurement of the redox potential indicates whether the water is in the so-called "reduced" or "oxidized" state. Water with a negative redox potential is often not directly suitable for use as drinking water, as it is free of oxygen and exhibits dissolved constituents such as hydrogen sulphide, organic substances, bivalent iron etc. Measured values in the clearly positive redox range indicate the presence of oxygen and in the case of redox potentials of, for example, greater than + 600 mV it can be expected that the water is sterile, as these high redox potentials are caused by powerful oxidants such as chlorine or ozone.

Measurement of the oxygen concentration in a water is particularly important as regards the water's technical and biological quality; the concentration can be established using chemical methods, although electrometric processes should be employed for preference. Electrometric measurement of oxygen concentrations is generally performed using a membrane-covered polarographic oxygen measuring cell. This cell contains two isolated electrodes, which are linked by means of an electrolyte in liquid or paste form and which are separated from the measuring medium (water) by means of a membrane which is permeable to oxygen. The temperature dependence of the oxygen measurement should be observed and the water must have a specific local velocity of current at the membrane for the purpose of the measurement. Even the simple modern apparatus fulfils these requirements. The manufacturer's instructions supplied with every set of apparatus should be observed with regard to calibrating the apparatus to zero and to the oxygen saturation point.

Battery checks and appropriate calibration of the measuring apparatus must be performed on the spot in the case of all electrometric methods used in the field for the purpose of water analys es.

2. Principles for simple microbiological water analysis

Attention is drawn in this context to Module 2.2 "Hygiene requirements for drinking water".

For the purpose of simple microbiological water analyses, determination of the so-called "colony count" in 1 ml of water, as well as the recording of and testing for fecal indicators such as Escherichia coli and coliform bacteria in 100 ml of water, is of considerable significance. If the latter cannot be detected in 100 ml of water, even under field conditions, and the general colony count for 1 ml is less than 100, the water can be regarded as acceptable under these conditions. In addition to these simple analyses, however, check analyses must always be performed on water samples which have been taken under sterile conditions and kept cool during transportation to the laboratory. The principle behind the simple microbiological water analyses discussed here is the fact that a germ capable of survival will, after a specific incubation period at a specified incubation temperature on a specific nutrient medium, develop into a colony which can be seen with the naked eye or with the aid of a magnifying glass. A variety of methods can be used for recording the colony count as well as for testing for Escherichia coli or coliform bacteria. The simplest methods, which experience has nevertheless shown to produce useful results permitting initial assessment of microbiological water quality, are summarized below.

As it is impossible under simple conditions to record the pathogenic organisms in a volume of water, the indicator principle is used. It is assumed that the water is acceptable from the microbiological point of view if fewer than 100 colonies develop under specific test conditions from 1 ml of the water and if neither Escherichia coli nor coliform bacteria are detected in 100 ml of the water. In the event of doubts which may arise, for example, on account of the origin of the water or in the course of a tour of the locality, more detailed microbiological analyses must be performed in an appropriately equipped laboratory, using correctly taken water samples which have been brought to the laboratory as quickly as possible.

2.1 Sterility (vessels, sampling, measurement etc)

It is clear that a microbiological analysis will yield useful results only if secondary infections of the water in question, caused by the sampling procedure and the vessels used, can be eliminated. For local analyses it is nowadays possible to obtain throwaway systems, which are packed so as to ensure sterility and which can be used directly. The instructions for use are to be strictly observed and it must be

ensured that no secondary infections can occur during sampling, e.g. through breathing on the samples or touching them with the fingers. The water for a microbiological analysis should be allowed to flow out at the sampling point for at least five minutes; the sampling point is then to be closed, subjected to a flame in a suitable way to kill off germs adhering to the outside and the water samples for the microbiological analysis subsequently taken after the water has been allowed to flow again for approximately one minute. If the water has to be drawn, the drawing vessels must be sterilized beforehand, e.g. by boiling them for at least five minutes in the water to be analysed. Other equipment used must also be sterilized, e.g. pipettes, filtering apparatus etc.

If the microbiological quality of the water is to be tested on the spot, the best testing apparatus is the simple equipment which is commercially available packed in plastic in sterilized form. If such apparatus cannot be obtained, all equipment and materials used for the local analyses must first be heat-sterilized or treated with solutions having a high chlorine content and subsequently rinsed with totally hygienic water until free of chlorine.

The most reliable method is to carry out the local analysis using equipment which has been sterilized in a suitable laboratory or to employ sterile ready-for-use products.

If samples are intended for microbiological analysis, they must - if the water is chlorinated - be mixed with sterile sodium thiosulphate solution in order to prevent the chlorine from having an effect during transportation. For the purpose of microbiological water analysis the samples must be taken to the analysis laboratory as quickly as possible and must be kept cool (approx. + 4°C) during transportation.

3. Methods for simple microbiological water analyses

Sections 3.1 to 3.3 below outline a number of simple microbiological water analysis methods which yield general values regarding the microbiological quality of the untreated or pure water in question, either directly on the spot or following transportation of the water samples (taken under sterile conditions) to a simple analysis laboratory, with the samples being kept cool during the journey.

3.1' Membrane filter methods or similar procedures (e.g. Sartorius or Millipore company)

Using suitable membrane filters with a mean pore size of around 0.45 µm, the microorganims in question can be separated from the water by means of filtration. If, for example, 100 ml of the water sample are filtered through a membrane filter of this type via suitable filtration apparatus, the microorganims are retained on the surface of the membrane filter. The filter - free of air bubbles - is then placed on a suitable solid nutrient medium and incubated for a specific time at a specific temperature. When testing for coliform bacteria the incubation temperature can be 35°C; for fecal coliform bacteria it should be 44.5°C. The incubation period is generally 24 hours, but can be increased to 48 hours.

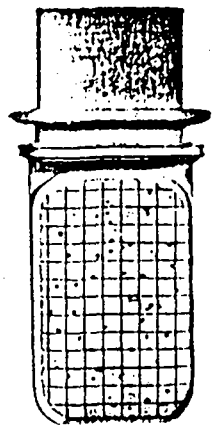
Placing of the membrane filter with the filtered-out microorganims on the nutrient medium or on cardboard culture discs ensures that the microorganism have an adequate supply of nutrients during the incubation period.

A highly simplified variation of the membrane filter system, which is nevertheless extremely suitable for local analyses under field conditions, takes the form of ready-for-use test devices. The inner, removable part of the device contains a membrane filter with a cardboard culture disc underneath. The water under analysis is then poured into the outer chamber up to the mark and the membrane filter insert with the cardboard culture disc placed in the chamber as a unit. After a specific time which is to be precisely observed, e.g. after 30 seconds, the water under analysis is poured out of the outer chamber, and the tester itself re-inserted in the empty chamber and incubated for 24 or 48 hours at 35°C or 44°C. The colonies which have then developed are counted. The general colony count which can be ascertained using this system is in relation to 1 ml of water. Escherichia coli and coliform bacteria can be recorded, likewise in 1 ml of water, using test kits specially equipped for detecting these types of bacteria (coli-count samplers), but such systems are suitable only in the case of severe infections. It is useful if a transportable battery-operated incubator is available for these analyses. Under extreme cinditions, however, it is also possible for a member of personnel to attach the devices to his own body, e.g. by means of a long scarf, and to take them with him into his sleeping bag in order to achieve the minimum incubation temperature of around 35°C.

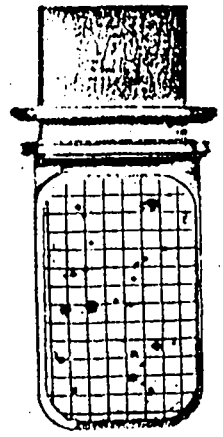
If it is possible to filter 100 ml of water through a 0.45 µm membrane filter under sterile conditions and subsequently incubate this filter on a nutrient medium, this method should always be preferred. The simple testers nevertheless yield useful general results on the spot. This applies in particular to the colony count. When testing for coliform bacteria, at least ten testers should be used for the same water sample in order to increase reliability.

An example of this type of tester is shown below.

Incubation and Interpretation



Fecal Coliform Colonies



Total Coliform Colonies

When the Coli-Count Sampler is used to test for *total coliforms*, it is incubated at 35°C for 18-24 hours. For *fecal coliforms*, the incubation temperature must be 44.5°C, controlled to within ±0.2°C for 18-24 hours.

Only colonies which are blue or blue-green in color* should be counted. Results are reported in colonies/100 ml. For example, 30 colonies counted:

$$\frac{30 \times 100}{\text{Sample volume (1 ml)}} = 3{,}000 \text{ coliforms/100 ml}$$

*Colonies only partly colored should also be counted as coliforms.

Basic working procedure:

Tot al colony count (red tester): Remove inner section using the handle (do not breathe on it or touch it etc), fill the container up to the mark with the water to be analysed, insert tester into container using the handle, shake a few times and leave in position for 30 seconds. Remove tester, pour out water and return tester to container. Incubate container at 35°C for 24 hours. Record all colonies which grow on the surface and which can be counted using the eye. Result to be specified in colonies/ml. If thinning was carried out as a result of too high a colony count, the thinning factor must be taken into consideration during evaluation.

When testing for coliform microorganisms, a similar procedure is to be adopted, using the blue tester and incubating the container for 18 to 24 hours at 35°C.

The same blue tester is to be used for determining the fecal coliform

microorganims; the incubation temperature, however, should be set to 44.5°C ± 0.2°C for a period of 18 to 24 hours. A transportable incubator should be used.

Only the colonies which are blue or blue-green in colour are counted following the incubation period. The results are given in colonies per 100 ml. If, therefore, 30 colonies are counted after the incubation period in accordance with the analysis specifications, this means that 30 must be mulitplied by 100, i.e. 3000 coliform microorganims were counted in a volume of 100 ml.

3.2 Tube methods

These involve, for example, systems (Hach) for recording the so-called total and fecal coliform bacteria counts in water. The tubes with the nutrient solutions and the accessories are supplied in sterilized form; suitable incubators for field analyses are likewise available.

This tube system too can be used without problems by a layman and, provided that the test specifications are observed, the tests for coliform microorganism will yield utilizable results under field conditions.

Every coliform test kit has an inner fermentation tube. If coliform bacteria grow during a test, the gas is caught in this tube and can be observed. This gas formation is a positive indication of the presence of coliform microorganims.

3.3 Plate methods

Plate methods are suitable for ascertaining the general colony count even under simple conditions. The nutrient media used consist of gelatine or agar. The gelatine nutrient media can be used only for incubation temperatures up to around 20 ± 2°C, whereas the agar nutrient media are suitable for 37°C and 44°C.

1 ml of the water to be analysed is added to and mixed with 10 ml of nutrient medium in liquefied form; the mixture is allowed to set and then incubated for the appropriate time. It is assumed that the spatial separation resulting after the nutrient medium has set means that each germ can form a colony separately from the others and that these colonies will develop given the appropriate temperature and incubation period. In general, the mesophilic aerobic bacteria are recorded at 20 ± 2°C,

while at 37°C ± 1°C it is also possible to determine microorganims significant from the point of view of hygiene. High colony counts, i.e. more than 100/ml at 20°C and over 20/ml at 37°C, indicate that the water in question has suffered secondary contamination, e.g. caused by human beings, animals or other organic loads.

If these simple microbiological water analyses yield results which are doubtful or cannot be clearly evaluated, despite the fact that the instructions for use accompanying the test kits were precisely observed, it is always advisable to have the analysis repeated in a suitable laboratory or, if this is impossible, to sterilize the water before consumption by boiling it or to carry out another suitable type of disinfection, e.g. chlorination.

4. Methods for physico-chemical and chemical water analyses

The methods used for simple physico-chemical and chemical water analyses were briefly outlined in Section 1. Analysis methods for a number of parameters which are also of significance for simple water analysis will now be described. Endeavours have been made to include one typical method from each of the basic technique categories referred to in Section 1. This selection therefore represents a set of examples rather than an evalution. Depending on the system available for simple water analyses in a particular location, the generally very simple analysis procedures, details of which are supplied by the manufacturer, must be strictly followed. Even untrained individuals can then perform useful measurements.

The theoretical considerations and the significance of the individual analyses are summarized in teaching module 0.3 "Basic concepts in water chmistry". It is recommended that the content of this module (3.2) should always be linked to that of modules 0.3 and 2.2, at least during the initial familiarization period.

4.1 Physico-chemical analysis including sensory test

4.1.1 Temperature

The temperature of the water is measured using a liquid-filled thermometer,

a mercury thermometer or an electric thermometer. The temperature is given in °C. The temperature should be read off once the reading has stabilized. A particularly useful instrument is the maximum-minimum thermometer, which can also be read out of the water. If the air temperature is measured after the water temperature, care must be taken to ensure that the thermometer is totally dry, as otherwise the evaporation cold will be included in the measurement.

4.1.2 Odour

Odour testing of water under field conditions is easy to carry out, preferably using a glass vessel, e.g. a glass bottle or flask. The water should be poured into the container until the latter is roughly two-thirds full; the container is then sealed and shaken, following which the person performing the test should smell the air above the suface of the water. If the water is cold, e.g. below 15°C, the impression of the odour can be increased by heating the water to around 20°C. The tester's impressions of the odour are to be expressed in generally understandable terms and it is also advisable to indicate the intensity; e.g. no odour, slight or strong odour, odours such as earthy, musty, putrid, manure-like, fishy, aromatic, chlorine odour, tar odour, phenolic, mineral oil odour, fuel-like, sulphurous, soapy etc. If the odour is so strong that the water cannot be drunk by human beings or animals, this should be noted.

4.1.3 Turbidity

In general, it is sufficient to assess turbidity on a qualitative basis. To this end, the water is poured into a glass vessel until the latter is around two-thirds full; the container is then shaken and the turbidity assessed against clear and dark backgrounds. The extent of turbidity can be described as follows: No turbidity, almost clear, slightly opalescent, slightly turbid, very turbid, opaque.

If the turbidity is assessed visually, it is also recommended to note its colour if any, e.g. according to the strength of the colour with terms such as colourless, very slightly coloured, slightly coloured and heavily coloured, and according to the shade of this colour, using terms such as yellowish, yellowish-brown, brownish-yellow, brown, light grey, dark grey, black, greenish, bluish, reddish etc (German standard water analysis methods).

4.1.4 Settleable substances

Only waste water or extremely turbid untreated water is generally analysed for settleable substances. For this purpose, so-called Imhoff cones are used. These are tapering containers made of glass or plastic, which can hold a litre of water and which have graduations in their lower tapering section. Water is poured in up to the one litre mark and the settleable substances read off in the lower graduated section after a waiting period of two hours. During this two-hour period the container should be abruptly rotated several times so that substances which have become deposited on the wall can settle. The measured values are given in ml/l after 2 hours.

4.1.5 pH value

Acidity (pH value) can be measured using indicator solutions, indicator paper or indicator tubes. For these colorimetric measurements, use is made of the colour change in an indicator or indicator mixture which responds to the pH value and conclusions drawn with regard to the pH value on the basis of this change in colour. Evaluation is either visual or by means of colour comparison in an appropriate comparator. Disturbances may occur if the water has a very high or very low salt content. Water which is itself coloured or which contains colloids may likewise impair colorimetric measurement of the pH value. The most reliable way of measuring the pH value is by means of electrometric methods. For this purpose, a probe is used in the form of a single-rod measuring chain, which consists of a glass electrode and a reference electrode, connected to a portable battery-operated or mains-operated pH meter. The measuring chain and the meter are calibrated using buffer solutions with a known pH value; the gradient of the meter reading is checked and adjusted using at least three buffer solutions at different pH values. The measuring range is generally between pH 1 and pH 10. Above pH 10 the so-called "sodium error" occurs; a sodium-resistant electrode must be used. The measuring chain must always be kept in water between measurements and the glass electrode must be cleaned and rinsed from time to time using a detergent solution.

4.1.6 Electrical conductivity

As already stated, this is a rough measure of the dissolved salts and

minerals contained in the water. The measured value is highly dependent on temperature, which means that the temperature must always be measured at the same time or a specific temperature set. Measured values can be compared with one another only if the water was in each case at an identical temperature or if the values were converted to the same temperature, e.g. 25°C.

Conductivity is measured using a conductivity meter and an appropriate immersion-type or flow-through type measuring cell, the former being almost always used for measurement in the field. Every measuring cell has a cell constant which is either specified on the cell or can be determined by means of calibration, e.g. using a potassium chloride solution with a known content. The working instructions provided by the equipment suppliers must be observed. Many meters can be set for conductivity ranges extending over several powers of ten. The conductivity is given in µS/cm or mS/cm at the respective temperature or in relation to 25°C. The measured value in µS/cm corresponds roughly to the concentration of dissolved ionizable substances in mg/l, while the value in millisiemens/cm corresponds to the concentration in g/l.

4.2 Chemical analyses

4.2.1 Oxygen

Quantitative determination of the oxygen dissolved in a volume of water can be carried out either by means of volumetric analysis according to Winkler or using the iodine difference method (German standard methods); it is also possible, however, to determine it electrometrically using a membrane electrode. It is the last-mentioned method which will now be briefly outlined here. Provided that the instructions for use supplied with the apparatus are observed, this is a very simple way of measuring the oxygen content of water. The measuring system comprises an indicator, an agitator and an oxygen membrane electrode acting as a single-rod measuring chain. The cathode is generally made of gold and the anode of a baser metal, e.g. silver. The electrode space is separated from the water by means of a membrane, e.g. made of Teflon. For the purpose of the measurement, the water must have a specific local velocity of current at the membrane; in many cases this is achieved by means of an agitator attached to the measuring chain. The apparatus must be calibrated to zero before the measurement is performed, using a so-called zero oxygen solution. This is a solution of around 3-5% sodium sulphite in water, which is totally free of oxygen. The oxygen saturation point is set - for example - by producing at 0°C a solution saturated with oxygen, which was obtained by stirring in air. In order to measure the oxygen content, the single-rod measuring chain is immersed in the water sample and the required local velocity of current produced by switching on the agitator. Air bubbles adhering to the electrode can be removed by briefly shaking it. As the oxygen content is temperature-dependent, the temperature of the water sample must be measured at the same time. The measured value is read off the measuring instrument once the reading has remained constant for around a minute. The oxygen content is read off directly in mg/l O_2.
Further information on chemical O_2 determination can be found in the GTZ's collection of water analysis methods.

4.2.2 Carbon dioxide (CO_2)

The carbon dioxide content can be determined by way of volumetric analysis. The term "carbon dioxide" is taken here to refer to the free dissolved CO_2; the term "free" represents the contrast to the CO_2 combined as hydrogen carbonates and carbonates and "dissolved" the contrast to the CO_2 rising in gaseous form. Direct titration of the CO_2 with sodium hydroxide solution and conversion into sodium hydrogen carbonate has proved a successful method in the field. The end point of the titration is at pH 8.3 and can be recognized either electrometrically using a glass electrode and a suitable pH meter or visually with the aid of phenolphthalein. This method is suitable for up to around 200 mg/l of free dissolved CO_2. In the case of a higher content the water should be diluted. If the water in question is very hard, e.g. over 28 mmol alkaline earth ions, or if it has a very high iron content, e.g. over 3 mg/l, it is advisable to add to the standard solution 2 ml of a 50% Seignette salt solution (potassium sodium tartrate) set to pH 8.3. Titration is performed using a titration burette until pH value 8.3 is reached or until the phenolphthalein changes from colourless to red. It is advisable to carry out preliminary titration and then - once the quantitative ratios are roughly known - to add the major proportion of the sodium hydroxide solution all at once, with the end point then being approached drop by drop. Further information may be found in the GTZ's collection of water analysis methods.

4.2.3 Chlorine

The available chlorine and the free available chlorine can be determined by way of volumetric analyses; in may cases, determination is via colorimetric or photometric methods using diethyl-p-phenylenediamine (DPD) or ortho-tolidine. This form of chlorine measurement is employed as a standard method practically all over the world, using simple comparators. A distinction is made between determination of the free available chlorine and of the combined available chlorine. The latter term refers to all chlorine compounds with an oxidizing effect, e.g. chloramines etc. The total of free chlorine and all chlorine substitution compounds with an oxidizing effect represents the available chlorine or total chlorine.

Procedure for determining free available chlorine: Using tweezers, a DPD reagent tablet without potassium iodide, as well as 1 to 2 ml of the water to be analysed, are placed in the cuvette. Once the tablet

has completely dissolved, the water to be analysed is poured into the cuvette up to the mark and the solution thoroughly mixed using a glass rod. The reference cuvette is filled with the water sample to be analysed without anything being added, and both cuvettes are placed in the comparator. The colour comparison disc is then turned until the colours are seen to be identical and the free chlorine content is read off in mg/l.

Determination of total chlorine: The analysis is performed in a similar manner to that described above, except that a DPD reagent tablet with added potassium iodide is used.

If the measured values are too high, i.e. outside the comparator's colour ranges, an aliquot part of the water sample should be diluted with distilled water and the analysis continued as described above. The dilution factor must be taken into account in the conversion.

Chlorine cannot be preserved, and must therefore always be determined directly on the spot. If significant chlorine contents are found, sterile sodium thiosulphate solution should be added to the water samples taken for the purpose of microbiological analysis so as to prevent the chlorine from having an effect on the microorganisms during transportation of the water samples.

4.2.4 Acid/base consumption, HCO_3^- and CO_3^{2-}

The acid consupmtion (alkalinity) of a water refers to the quantity of a strong acid in mval/l consumed during titration until specific pH values are reached or until specific indicators change colour. If this titration is carried out electrometrically as far as pH 8.3 or using phenolphthalein as an indicator, the acid consumption is represented by the so-called "p-value". If the titration is continued as far as pH 4.3 or using methyl orange or a mixed indicator which changes colour in this pH range, the acid consumption takes the form of the m-value.

In the same way, the base consumption (acidity) of an acid volume of water represents the titration value with sodium hydroxide solution.

If the titration is carried out electrometrically as far as pH 4.3 or using methyl orange or a mixed indicator, the base consumption is obtained in the form of the negative m-value. If the titration is performed electrometrically as far as pH 8.3 or using phenolphthalein as

an indicator, it is obtained in the form of the negative p-value. The acidity of a natural water is essentially caused by dissolved carbon dioxide (CO_2). Humic acids or other weak organic acids, however, may also be involved. In such cases, the pH values of the water are around pH 4.3. If mineral acids are present, the pH value may drop to below 4. The measured pH value thus already provides an indication.

Determination of p-value and m-value: A few drops of phenolphthalein solution are mixed with 100 ml of the water sample. If the solution then turns red, titration is performed with 0.1 n hydrochloric acid until the colour disappears. The ml of 0.1 n hydrochloric acid used correspond to the p-value and thus essentially to the carbonates (Ml 0.1 n hydrochloric acid x 30 = mg CO_3^{2-}/l).

0.1 ml of a mixed indicator is then added to the titrated solution and titration continued with 0.1 n hydrochloric acid. The colour changes from blue-green to grey and then to red if the Mortimer mixed indicator is used. The ml of 0.1 n hydrochloric acid used correspond to the m-value and can be used to determine the hydrogen carbonates (ml 0.1 n hydrochloric acid x 61 = mg HCO_3^-/l).

In the case of more acidic water, titration is performed - using 0.1 n sodium hydroxide solution - until the negative m-value and negative p-value are reached (see also 3.2.2).

The GTZ's collection of water analysis methods should be consulted as regards determination of the so-called lime aggressivity and of the lime dissolving power.

4.2.5 Hardness

Although the term "water hardness" is obsolete and also inadequately defined, it is still frequently used. The hardness of water is caused by the alkaline earth ions dissolved in the water, i.e. magnesium, calcium and strontium. This so-called "total hardness" is generally determined today using complexometric methods. The so-called "carbonate hardness" corresponds to the hydrogen carbonate ions which can be attributed to calcium, magnesium and strontium. The m-value of the water multiplied by 2.8 yields the proportion of carbonate hardness, attributable to the hydrogen carbonate ions. There are cases, however, in which the carbonate hardness exceeds the total hardness; in such cases alkali hydrogen carbonates are present in the water and the carbonate hardness can be equated with the total hardness.

The non-carbonate hardness is normally calculated by subtracting the carbonate hardness from the total hardness. The relationships between the various degrees of hardness commonly used throughout the world and the measured values in mmol/l or mval/l can be seen from the conversion table below.

Conversion table (Alkaline earth ions Mg, Ca and Sr)

	Alkaline earth ions mmol/l	Alkaline earth ions mval/l	German degree °d	US hardness ppm $CaCO_3$	British degree °e	French degree °f
1 mmol/l alkaline earth ions	1.00	2.00	5.60	100.0	7.02	10.00
1 mval/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 British 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

Determination of the total hardness as the total of the alkaline earths magnesium, calcium and strontium in the water is carried out by means of complexometric methods, using a mixed indicator in liquid or tablet form. The colour change is from red through grey-green to green.

In addition to tablets, a dropper can also be used, with, for example, one drop corresponding to one °d, i.e. 10 mg CaO/l, or a titration pipette can be employed. To this end, the measuring vessel is pre-rinsed with the water under analysis and then filled up to 5 ml mark. Once three drops of indicator solution have been added and mixed in, the sample turns red. Using the titration pipette set to 0°d with standard solution, the titrant is added to the water sample in drops until the colour changes from red through grey-violet to green. The total hardness of the water can then be read off directly from the titration pipette scale, e.g. in German degrees of hardness or in ppm $CaCO_3$ (US degrees oh hardness).

The total hardness less the so-called carbonate hardness yields the non-carbonate hardness, i.e. the proportion of magnesium, calcium and strontium ions attributable to the anions chloride, nitrate and sulphate.

4.2.6 Calcium/Magnesium

The individual determination of calcium and magnesium alongside each other is possible using complexometric methods. The ready-for-use analysis systems generally offer the opportunity to determine the calcium and the total hardness, so that the magnesium can be determined by way of subtraction. Direct calcium determination is possible on the spot by means of titration using Komplexon III solution and Calgon carboxylic acid as an indicator.

2.5 g of potassium hydroxide (caustic potash) or 5 ml of diethylamine are added to 100 ml of the water under analysis. The magnesium precipitates and the solution attains a pH value of around 12. 5 to 10 drops of indicator solution (Calgon carboxylic acid) are added and titration carried out - with the container being shaken - using 0.1 mol Komplexon III solution until the colour changes from claret to blue. 1 ml of 0.1 mol Komplexon III solution corresponds to 4.008 mg Ca^{2+}. Komplexon III solution corresponds to Titriplex III solution.

Calcium in water samples can also be determined by colorimetric or photometric means, e.g. using the cuvette test system.

4.2.7 Iron

a) A very simple test for iron can be performed by pouring around 100 to 500 ml of water into a glass bottle so that it is around half full and then shaking it such that air is included. After it has been left to stand for a specific time, e.g. one hour, very slight yellow turbidity and small yellowish-brownish flocs form if the iron content is between 0.1 and 1 mg/l. If the iron content is in excess of 1 mg/l, the water becomes noticeably yellowish-brownish and brownish flocs are in evidence. In the case of an iron content exceeding 10 mg/l the water becomes extremely brown and a brown sediment forms.

b) Colorimetric determination of iron (example: Aquamerck method):

Principle: The iron in a water sample takes the form of dissolved iron (Fe^{2+}) and undissolved iron (Fe^{3+}). To determine the total iron content, Fe^{3+} is dissolved, reduced to Fe^{2+} and coloured, e.g. using 1,1'-bipyridine or 1,10-o-phenalthroline. The dissolved Fe^{2+} is directly coloured and the colour comparison performed.

Determination of total iron (Fe^{2+} and Fe^{3+})

1. Rinse test vessel several times with the water under analysis and then fill it as far as the upper mark (corresponds to 10 ml).
2. Add six drops of reagent 1.
3. Add six drops of reagent 2.
4. Add six drops of reagent 3.

After each addition of reagent, seal test vessel with lid and shake well.

5. Total iron content in mg/l (ppm) is determined ten minutes after the addition of reagent 3 by matching the red colour of the reaction solution to the appropriate level in the colour scale.

Determination of bivalent iron (Fe^{2+})

1. Rinse test vessel several times with the water under analysis and then fill it as far as the upper mark (corresponds to 10 ml).
2. Add six drops of reagent 2.
3. Add six drops of reagent 3.

Shake well after each addition of reagent

4. The Fe^{2+} content is determined as described above ten minutes after reagent 3 has been added.

Determination of trivalent iron (Fe^{3+})

The Fe^{3+} content is determined by subtracting the bivalent iron from the total iron.

4.2.8. Manganese (Visocolor, Macherey-Nagel & Co, manganese test kit)

Principle: Manganese ions of every valence stage react in an aqueous alkaline solution with formaldoxime and form an orangy-red complex dyestuff. The measured values can be estimated roughly in the range between 0.1 and 4 mg of manganese per 1 litre.

Instructions for use:

1. Rinse comparator cuvette several times with test solution and fill up to the mark (9 ml).
2. Add five drops of reagent 1 and mix.
3. Add five drops of reagent 2 and mix. Wait one minute.
4. Add five drops of reagent 3 and mix.
5. Add a few crystals of reagent 4 and mix. After five minutes, hold comparator against the light at eye level, with the rough side facing towards the rear, and match the colour of the solution to the corresponding colour field; read off Mn content. In the case of very small quantities of manganese, hold a sheet of white paper behind the comparator in order to facilitate the reading.

4.2.9 Ammonium (Aquamerck)

Principle: Water becomes yellowish-brownish following addition of Nessler's reagent. Measuring range approx. 0.1 to 5 mg/l.

Instructions for use:

1. Rinse measuring vessel with the water under analysis and fill up to the 5 ml mark.
2. Add in succession three drops each of reagent solutions 1, 2 and 3. Shake well after adding each solution.
3. Place measuring vessel on the white centre strip of the ammonium colour scale and move it until the colour of the solution coincides with one of the ammonium colour comparison values or until it can be classified between two colour comparison values (look through the solution from above).
4. After five minutes, read off ammonium concentration in mg/l (ppm).

4.2.10 Nitrite (Visocolor)

Principle: Formation of a red dyestuff which is evaluated using colorimetric methods. Measuring range 0.05 to 2 mg/l of water.

Instructions for use:

1. Rinse comparator cuvette several times with test solution and fill as far as the lowest mark (8 ml).
2. Add reagent 1 as far the middle mark (1 ml).
3. Add reagent 2 as far as the upper mark (1 ml) and mix.
4. After five minutes, hold comparator against the light at eye level, with the rough side facing towards the rear, and match the colour of the solution to the corresponding colour field. Read off NO_2^- content (ppm = mg/l). In the case of very small quantities of NO_2^-, hold a sheet of white paper behind the comparator in order to facilitate the reading.

4 2.11 Nitrate (Merckoquant - nitrate test rods, packs of 50)

Principle: Nitrate determination in the absence of nitrite ions. Immerse test rods in the water for approximately 10 seconds, remove and then read off colour formed, doing so after no less than two minutes and no more than three minutes. The simple colour graduations can indicate a content of approximately 5, 10, 30 or 100 mg/l.

If the test rods remain exposed to the air for more than three

minutes following immersion in the water, an interference colour may form which cannot be evaluated.

4.2.12 Chloride (Aquamerck)

Principle: Titration of the chloride with mercury (II) nitrate and diphenylcarbazone as indicator.

Instructions for test using dropping bottle:

1. Rinse measuring vessel with the water under analysis and fill as far as the 5 ml mark.
2. Add two drops of reagent 1 and shake well. The solution generally turns blue at this point.
3. While continuing to shake the container, add reagent 2 in drops until the colour changes to yellow.
4. Add reagent 3 from the dropping bottle in drops until the colour of the water sample changes from yellow to violet. Keep the dropping bottle vertical and carefully swing the reaction vessel round after each drop. Count drops. 1 drop = 25 mg/l Cl^-.

4.2.13 Sulphate

Simple determination of sulphate content can be performed within a measuring range from 10 to 150 mg sulphate/l using, for example, the so-called "cuvette test" from Dr. Lange. This involves measuring the barium sulphate turbidity following the addition of barium chloride. Principle: 5 ml of the water sample are mixed with barium chloride, shaken and the barium sulphate turbidity measured in a photometer.

To provide a rough guideline, 100 ml of water can also be acidified with hydrochloric acid and mixed with approx. 5% barium chloride solution until maximum turbidity is reached. The intensity of the turbidity is then to be compared with aqueous solutions with a known sulphate content in graduations e.g. of 10, 50 and 100 mg/l which have been treated in the same way.

4.2.14 Organic substances

It is almost impossible to determine the organic substances in water samples using simple means. They are generally ascertained by way of oxidation with potassium permanganate in an acid or alkaline solution (potassium permanganate consumption) or in the form of chemical oxygen demand (COD) by means of oxidation of the organic compounds with potassium dichromate in a solution with a high sulphuric acid content and at a high temperature.

A simple field test for organic substances can be performed by evaporating the water and gently heating the evaporation residue. If substantial quantities of organic substances are present, the evaporation residue will turn yellow or brown to a greater or lesser extent.

It is also possible to mix the water sample with sulphuric acid (1 + 1) until a strongly acid reaction is obtained (pH paper) and then to boil it for around ten minutes. If substantial quantities of organic substances are present, the water sample containing sulphuric acid will take on a yellowish or brownish tinge.

To summarize, it should be pointed out once again that an attept has been made in this Section 3.2 to describe as examples a number of methods which can be used for the purpose of water analysis under field conditions or in a simply equipped laboratory. It is advisable to obtain information from the firms listed at the beginning of the module and to select the system which is most appropriate for the tasks on hand, or alternatively to purchase a largely self-contained portable water analysis laboratory such as is offered, for example, by Hach, Merck, Macherey-Nagel or VDSF.

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0.3 Basic concepts of water chemistry
0.4 Basic principles of water transport
1.1 The function and technical composition of a watersupply system
1.2 Organisation and administration of waterworks

Special Knowledge

2.1 Engineering, building and auxiliary materials
2.2 Hygienic standards of drinking water
2.3a Maintenance and repair of diesel engines and petrol engines
2.3b Maintenance and repair of electric motors
2.3c Maintenance and repair of simple driven systems
2.3d Design, functioning, operation, maintenance and repair of power transmission mechanisms
2.3e Maintenance and repair of pumps
2.3f Maintenance and repair of blowers and compressors
2.3g Design, functioning, operation, maintenance and repair of pipe fittings
2.3h Design, functioning, operation, maintenance and repair of hoisting gear
2.3i Maintenance and repair of electrical motor controls and protective equipment
2.4 Process control and instrumentation
2.5 Principal components of water-treatment systems (definition and description)
2.6 Pipe laying procedures and testing of water mains
2.7 General operation of water main systems
2.8 Construction of water supply units
2.9 Maintenance of water supply units Principles and general procedures
2.10 Industrial safety and accident prevention
2.11 Simple surveying and technical drawing

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3.3b Design and working principles of electric motors
3.3c –
3.3d Design and working principle of power transmission mechanisms
3.3e Installation, operation, maintenance and repair of pumps
3.3f Handling, maintenance and repair of blowers and compressors
3.3g Handling, maintenance and repair of pipe fittings
3.3h Handling, maintenance and repair of hoisting gear
3.3i Servicing and maintaining electrical equipment
3.4 Servicing and maintaining process controls and instrumentation
3.5 Water-treatment systems: construction and operation of principal components: Part I - Part II
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3.7 Inspection, maintenance and repair of water mains
3.8a Construction in concrete and masonry
3.8b Installation of appurtenances
3.9 Maintenance of water supply units Inspection and action guide
3.10 –
3.11 Simple surveying and drawing work

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