

**W.Fresenius K.E.Quentin  
W.Schneider (Eds.)**

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# **Water Analysis**

**A Practical Guide to Physico-Chemical,  
Chemical and Microbiological Water Examination  
and Quality Assurance**



**Springer-Verlag**

W. Fresenius K. E. Quentin  
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# Water Analysis

A Practical Guide to Physico-Chemical,  
Chemical and Microbiological Water Examination  
and Quality Assurance

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# Foreword

1977 saw the publication of "A Collection of Methods for Water Analysis", a three-volume work in ring-binder form compiled by W. Fresenius and W. Schneider for the GTZ (Deutsche Gesellschaft für Technische Zusammenarbeit), 6236 Eschborn 1, FRG. This publication was geared to the needs of a project in Algeria.

More recently, the editors were requested by the GTZ to produce, on the basis of the previous collection of the water analysis methods, which was published in French, an updated and revised version to be used in different partner countries and for publication in 1985/86. This was not only to take account of advances in water analysis and instrumental techniques, but also to include simple methods of analysis for use in the field, and methods suitable for use in laboratories with relatively unsophisticated equipment.

The approach envisaged by the GTZ was to divide up information on water, water supplies and water analysis into three broad groups, namely:

1. Simple modules on the physics and chemistry of water, water hygiene and water analysis capable of being understood and applied in practice by the layman using suitable chemicals and equipment (W. Schneider).
2. Information to supplement work by Rump-Krist, also commissioned by the GTZ, on water analysis methods which could be used in laboratories with simple equipment, particularly in the Third World (Verlag Chemie, Weinheim, FRG, 1986).
3. In addition to detailed instructions on sampling methods and on-the-spot analysis of water, the new work, "Water Analysis (A Practical Guide)", was also to provide a concise theoretical presentation of the various techniques of water analysis together with an indication of their relative importance, and to describe methods for use in water analysis laboratories with simple equipment or the latest in modern facilities. It was to include an account not only of up-to-date analysis methods, eg. tests for anthropogenic traces of organic and inorganic substances, but also biological approaches to water analysis. And finally it was to comment on the mathematical evaluation and weighting of the data obtained from water analysis, and to make it possible to arrive at a comparative appraisal of the findings in the light of new guidelines and rules on the quality of wastewater, surface water, ground water, drinking water etc.

One major consideration in this work has been the GTZ's desire to provide its counterparts and their analytical laboratories with summaries of analytical methods which have been tried and tested in practice, and were necessary to give theoretical and practical explanations of these methods, in order to permit laboratories with equipment of varying degrees of sophistication to handle the monitoring of the water quality. Information was also to be included to facilitate appraisal of the significance of analytical findings by comparison with legislation or guidelines from a number of different countries.

The editors and the individual contributors have amassed a broad range of experience of water analysis in virtually every part of the world. The choice of methods for determining the various parameters in water samples is the product of the experience and the results of individual laboratory work in Germany. This book thus embodies not only the author's and editor's practical experience with regard to feasibility of water analyses, but also the experience they have gained during periods of work overseas. Personal experience of the feasibility of the various methods in practice has been a key criterion in the selection of items for inclusion.

In the context of the International Water Decade 1981–1990 the GTZ felt there was a need for a comprehensive contribution of this kind to the field of water analysis and hence to the problem of assuring the quality of water, especially drinking water.

The editors and contributors would like to express their gratitude to Mr. Betz, Mr. Deichsel, Mr. Eichner, Mr. R.E. Fresenius, Mr. Frimmel, Mr. Golwer, Mr. Maushart, Mr. Scholz and Mr. Guckes for their contributions and advice, and to Mrs. Wienrich and Mrs. Bibo for their expert assistance. Our thanks are also due to the typists, Mrs. Wagner and Miss Haas, to Mrs. Fischer and Mrs. Krist for the drawings etc. We should particularly like to thank Mr. Kresse, head of GTZ's "Water Supply and Sanitation" Section, as well as Mrs. Zeumer and Mrs. Tazir of the GTZ Translation Service and the translators involved in producing the English text. Special thanks also go to Mr. T. Oliver for monitoring the English text and Mrs. M. Masson-Scheurer for the final type-script.

The editors and contributors hope that this work, "Water Analysis (A Practical Guide)", will provide water analysts in responsible positions with a valuable guide to assist them in their task of training staff to carry out local inspections and take samples, performing both simple and advanced analysis and assessing the significance and implications of analytical findings. If the book comes anywhere near achieving this ambitious purpose, it will be endorsement enough of its claim to have been produced by practitioners for practitioners.

Constructive criticism from colleagues is always welcome.

We should like to conclude with the hope that future water analysts, not to mention water technologists, will find this book useful in their studies at technical institutions and universities, especially in those countries involved in cooperation with the Federal Republic of Germany.

W. Fresenius  
K. E. Quentin  
W. Schneider

# Preface

This GTZ publication, "Water Analysis (A Practical Guide to Physico-Chemical, Chemical and Microbiological Water Examination and Quality Assurance)", belongs to the wide range of publications for the water sector within the scope of the International Decade for Drinking Water Supply and Sanitation.

The publication responds to the requirements for information and further training in the Federal Republic of Germany's partner countries in technical cooperation projects. It reflects the experience gathered in projects for monitoring and improving water quality, e.g. through establishing national environmental laboratories and water works laboratories for monitoring drinking water quality.

In the growing concern for our environment, maintaining water quality standards and protecting natural water resources have assumed key significance, particularly in newly industrialising countries and Third World conurbations.

Excessive strains on the environment, such as intensive farming, industry and centres of high population density, rapidly inflict serious damage both on the ecological balance and – a fact which often fails to be acknowledged due to a lack of monitoring methods – on human beings.

This publication provides those engaged in monitoring and environmental laboratories, waterworks laboratories and also in research and teaching with reliable and recognized techniques of day-to-day analysis and assessment, in order to develop sound monitoring systems and effective measures for protecting and improving water quality.

The GTZ wishes to thank the authors – in particular Prof. W. Schneider for his untiring efforts – and also the translators, and hopes that "Water Analysis" will be disseminated throughout the world.

Eschborn, September 1987

Dr. Ing. Klaus Erbel  
Head of Division  
GTZ "Hydraulic Engineering/  
Water Resources Development"

# Literature

## I Basic Literature

- Fachgruppe Wasserchemie in der GDCh (Ed) (1986) Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchungen, VCH Verlagsgesellschaft, 6940 Weinheim, FRG
- DIN, Deutsches Institut für Normung eV (1986) Beuth-Verlag, Berlin, FRG
- ISO – International Organization for Standardization 1986 and Draft International Standards ISO Water Quality – Physical, Chemical, Biochemical, ISO, 1211 Geneva, Switzerland
- American Public Health Assoc (Ed) (1979) Standard Methods for the Examination of Water and Wastewater. 16th Ed, Washington, DC, USA
- ASTM (1984) Annual Book of ASTM Standards, Part 31: Water. American Society for Testing and Materials, Philadelphia, PA, USA
- United States Environmental Protection Agency (1979) Methods for Chemical Analysis of Water and Wastes, USEPA, Cincinnati, OH, USA
- World Health Organization (1984) Guidelines for Drinking-Water Quality, vol 1–3, WHO, 1211 Geneva, Switzerland
- FAO (Ed) (1986) Codex Alimentarius, Methods of Analysis for Natural Mineral Waters. Food and Agriculture Organization of the United Nations, Rome, Italy
- Suess MJ (Ed) (1982) Examination of Water for Pollution Control, vol 1–3 Pergamon Press, Oxford (World Health Organization), UK
- Rodier J (1978) L'analyse de l'eau. Eaux naturelles, eaux résiduaires, eau de mer. 6me ed Dunod, Paris, France
- Institut für Wasserwirtschaft (Ed) Ausgewählte Methoden der Wasseruntersuchungen, Vol 1 (1986), Vol 2 (1982). VEB G. Fischer Verlag, Jena, GDR
- Hutton L (1983) Field Testing of Water in Developing Countries, Water Research Centre, Medmenham, UK
- Sontheimer H, Spindler P, Rohman U (1980) Wasserchemie für Ingenieure, DVGW Forschungsstelle, Karlsruhe, FRG
- Souci SW, Quentin KE (Ed) (1969) Handbuch der Lebensmittelchemie, Band VIII/1 und 2: Wasser – Wasser und Luft, Springer Verlag, Heidelberg-Berlin-New York, FRG
- Fachgruppe Wasserchemie in der GDCh/Normenausschuß CNAW-Wasserwesen im DIN Jahrbuch „Vom Wasser“, 1975–1986. Verlag Chemie, 6940 Weinheim, FRG
- Cheeseman R, Wilson A (1978) Manual on Analytical Quality-Control for the Water Industry. Water Research Centre, Stevenage, UK
- Förstner U, Wittman G, (1981) Metal Pollution in the Aquatic Environment, Springer Verlag, Berlin-Heidelberg-New York, USA
- Stumm W, Morgan J (1981) Aquatic Chemistry. John Wiley & Sons, New York-Chichester

- GTZ (Ed) Fresenius W, Schneider W (1979) Méthodes pour l'analyse des eaux, vol 1-3, GTZ, 6236 Eschborn, FRG
- GTZ (Ed) Schneider W (1980) Technologie de l'eau potable. GTZ, 6236 Eschborn, FRG
- GTZ (Ed) Fresenius W, Schneider W, Boehnke B, Poeppinghaus K (1984) Abwassertechnologie. Springer Verlag, Berlin-Heidelberg-New York-Tokyo, FRG
- GTZ (1985) Water Modules, GTZ, 6236 Eschborn, FRG
- GTZ (Ed) Rump HH, Krist H (1986) Manual for the Examination of Water, Wastewater and Soil, VCH Verlagsgesellschaft, Weinheim-Deerfield Beach FL, FRG/USA
- Höll K (1986) Wasser, 7. Auflage. Walter de Gruyter, Berlin-New York, FRG
- Huetter LA (1984) Wasser und Wasseruntersuchung, Verlag Diesterweg-Salle-Sauerlaender-Frankfurt-Berlin-München-Aarau, FRG
- E. Merck. (1980) Die Untersuchung von Wasser, 6100 Darmstadt, FRG

## II Monographs

- Welz B (1986) Atomic Absorption Spectrometry, 2nd Ed VCH Verlagsgesellschaft, Weinheim-Derfield Beach FL, FRG/USA
- Snell FD (1978) Photometric and Fluorometric Methods of Analysis, vol 1-3. John Wiley & Sons, New York-Chichester
- Kissinger PT, Heineman WR (Eds) (1984) Laboratory Techniques in Electroanalytical Chemistry. Marcel Dekker, New York-Basel, USA
- Gasparic J, Churacek J (1978) Laboratory of Paper- and Thin-Layer Chromatography. Horwood – Wiley J, New York-London-Chichester, UK
- Engelhardt H (1979) High Performance Liquid Chromatography. Springer-Verlag, Belin-Heidelberg-New York, FRG
- Kraft G, Fischer J (1972) Indikation von Titrationen. Walter de Gruyter, Berlin-New York, FRG
- Wang J (1985) Stripping Analysis, VCH Verlagsgesellschaft, Weinheim-Deerfield Beach FL, FRG/USA
- Hachenberg H, Schmidt AP (1972) Gas Chromatographic Headspace Analysis. Heyden, London-New York-Rheine, UK/USA/FRG
- Grob RL (1985) Modern Practice of Gas Chromatography, 2nd Ed John Wiley & Sons, New York-Chichester
- Bertsch W, Jennings WG, Kaiser RE (1982) Recent Advances in Capillary Gas Chromatography. John Wiley & Sons, New York-Chichester
- Seelmann-Eggebert W, Pfennig G, Muenzel H (1974) Chart of the Nuclides. Verlag Gersbach & Sons, Munich, FRG
- Haberer K (1962) Radionuclide im Wasser. Thiemic Verlag, Munich, FRG
- Handbook of Elektrode Technology, Orion Research – Colorameßtechnik, 7073 Lorch, FRG

## III Journals

- Analyst RSC, London, UK
- Analytical Chemistry, ACS, Washington DC, USA
- Analytica Chemica Acta, Elsevier, Amsterdam, Nederland
- Fresenius Zeitschrift für Analytische Chemie, Springer Verlag, Berlin-Heidelberg-New York-Tokyo, FRG

Atomic Spectroscopy, Norwalk CT, USA

Water Research, Pergamon Press, Oxford-New York, UK/USA

Journal American Water Works Association, New York, USA

Int J Environmental Analytical Chemistry, Gordon and Breach, New York-London-Tokyo

Gesundheitsingenieur, Oldenbourg Verlag, Munich, FRG

Journal for Water and Wastewater Research, VCH Verlagsgesellschaft, Weinheim, FRG

Gas- und Wasserfach – Wasser-Abwasser, Oldenbourg Verlag, München, FRG

Forum Städte-Hygiene, Patzer Verlag, Hannover-Berlin, FRG

Wasser, Luft und Betrieb, Vereinigte Fachverlage Krausskopf, 6500 Mainz, FRG

Labo, Hoppenstadt, 6100 Darmstadt 1, FRG

Zentralblatt für Bakteriologie, Mikrobiologie und Hygiene, G. Fischer Verlag, 7000 Stuttgart, FRG

GIT-Verlag, 6100 Darmstadt 11, FRG

International Labmate Newgate, Sandpit Lane St. Albans, Herts, UK

Water Research, Pergamon Preß, 6242 Kronberg, FRG

Applied Atomic Spectrometrie, Perkin Elmer Corp Analytic Instruments, Main Ave. Norwalk CT 06856, USA

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