Examination of Water for Pollution Control

A REFERENCE HANDBOOK

IN THREE VOLUMES

VOLUME 3
Biological, Bacteriological and Virological Examination

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MICHAEL J. SUESS

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MICHAEL J. SUESS
World Health Organization
Regional Office for Europe, Copenhagen, Denmark

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Cover: Biological sampling (photo WHO/M. Jacot). Colonies of faecal streptococci (courtesy of Karin Ormerod, Norwegian Institute of Water Research, Oslo); human adenovirus (courtesy of Robert W. Horne, John Innes Institute, Norwich, U.K.)

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PREFACE

The older industrialized countries experienced gross pollution of water, air and soil for many years before either the political will or the technical means existed for effective control. Nevertheless, in some of these countries, substantial steps were being taken to carry out improvements as early as the beginning of the century and in the field of water pollution, for example, many biological treatment plants still in operation were constructed over half a century ago.

Countries which have experienced rapid industrialization more recently have had more technical experience to draw on, but have often had to face pressures to maintain or improve the quality of the environment in a much shorter time.

During the last few years, there has been an increasing realization that water resources are limited and must be conserved, leading to the necessity for stringent quality control.

Many of the communicable diseases having the greatest impact on mankind are waterborne, and a permanent reduction in morbidity and mortality can most effectively be achieved by providing safe drinking-water and satisfactory sanitation. It is the ambitious target of the International Drinking-Water Supply and Sanitation Decade that such facilities will be available for all communities in the world by 1990. This programme fits well into the World Health Organization's increased emphasis on the preventative approach to health care. The investment will be largely wasted unless it embodies the development of systematic water quality surveillance.

In addition to the long-standing problem of microbiological pollution, the introduction to the environment of an increasing range of chemicals has led to the need for ever more complex technologies for surveillance and control.

Effective water quality management involves systematic programmes of sampling and analysis of rivers, lakes and groundwater and all stages of waste treatment. Proven and harmonized procedures must be adopted if results are to be reliable, reproducible and comparable.

The present Handbook has been developed by the WHO Regional Office for Europe with these objectives in mind. It has involved the active cooperation of many institutions and over 250 scientists in 31 countries, over a period of 10 years. It is primarily intended for routine use in relation to process control and surveillance programmes, but it is hoped that it will also be useful both for research and in training laboratories.

Many countries share common water resources and an increasing number of countries are now adopting similar systems of pollution monitoring and control, through various forms of international agreements. It has been the intention of all concerned in the development of the Handbook that its adoption should help such cooperation by facilitating the harmonization of sampling and analytical procedures throughout the world.

On behalf of WHO, I should like to thank all concerned in its production.

J. IAN WADDINGTON

Director, Promotion of Environmental Health,
WHO Regional Office for Europe

CONTENTS OF OTHER VOLUMES

NOTE ON TERMINOLOGY

WHO policy in respect of terminology is to follow the official recommendations of authoritative international bodies such as the International Union of Pure and Applied Chemistry (IUPAC) and the International Organization for Standardization (ISO). Every effort has been made in this publication to comply with such recommendations.

Nearly all international scientific bodies have now recommended the use of the SI units (*Système international d'Unités*) developed by the Conférence générale des Poids et Mesures (CGPM),[a] and the use of these units was endorsed by the Thirtieth World Health Assembly in 1977. In almost all cases, only SI units are used in this publication. However, the use of the curie (Ci) instead of the becquerel (Bq) has been retained in radiological texts (1 mCi = 37 MBq).

As the base unit "amount of substance", the CGPM has adopted the mole. As a result, the variable units "equivalent" and "normality" are inconsistent with the international system. Confronted with this problem, the 29th IUPAC General Assembly in 1977 officially abandoned the use of "equivalent" and "normality" and approved a new terminology to replace them. Subsequently a joint IUPAC–ISO *ad hoc* group made detailed recommendations for implementing this new terminology. A new physical quantity named "equivalent entity" has been defined, and since it is a physical quantity and not a unit, the fact that it may vary according to the particular reaction in which an acid, a base, or an oxidizing or reducing agent participates is of no consequence.

The unit in which equivalent entity is expressed is the mole, or an appropriate multiple or submultiple. Concentrations of acids, bases, and oxidizing or reducing agents are therefore expressed in $mol \cdot m^{-3}$ or an appropriate multiple or submultiple, such as $mol \cdot l^{-1}$ or $mmol \cdot l^{-1}$. These units replace "normality" as well as such units as $mEq \cdot l^{-1}$.

[a] An authoritative account of the SI system entitled "The SI for the Health Professions" has been prepared by the World Health Organization and is available, through booksellers, from WHO sales agents, or direct from Distribution and Sales Service, World Health Organization, 1211 Geneva 27, Switzerland.

EXAMPLES

1. Acid–base reaction

In the reaction

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

$\frac{1}{2}$ mole of H_2SO_4 is equivalent to 1 mole of NaOH, i.e., the equivalent entities are ($\frac{1}{2}$ H_2SO_4) and (NaOH). The substance concentration of sulfuric acid is written as $c(\frac{1}{2}\ H_2SO_4)$, e.g. $c(\frac{1}{2}\ H_2SO_4) = 0.1\ mol \cdot l^{-1}$, instead of H_2SO_4, 0.1N solution.

2. Redox reaction

In the reaction

$$5FeSO_4 + KMnO_4 + 4H_2SO_4 = \tfrac{1}{2}K_2SO_4 + MnSO_4 + 5/2Fe_2(SO_4)_3 + 4H_2O$$

each reacting entity of ($5FeSO_4$) is equivalent to one of $KMnO_4$ at the equivalence point. Five electrons are transferred in the reaction:

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

$$5Fe^{2+} = 5Fe^{3+} + 5e^-$$

and the equivalent entities of iron(II) sulfate and potassium permanganate are ($FeSO_4$) and ($1/5\ KMnO_4$). The substance concentration of potassium permanganate is therefore written as $c(1/5\ KMn0_4)$, e.g. $c(1/5\ KMnO_4) = 0.1\ mol \cdot l^{-1}$, instead of $KMnO_4$, 0.1N solution.

It should also be noted that all substance concentrations are expressed in the form $mol \cdot l^{-1}$, $g \cdot l^{-1}$, $mg \cdot kg^{-1}$, etc., the denominator being always the litre or the kilogram. Such expressions as p.p.m., %(w/v), and g% are no longer in conformity with the recommendations of international scientific organizations.

It will be noted that when the new definition of equivalent entity as a quantity (rather than unit) is used, there is no change in the numerical values traditionally associated with the concept of " normality ".

INTRODUCTION

Pollution of water affects the lives of a great many people throughout the world, especially those living in industrialized areas. Moreover, the organic and inorganic pollution load in natural waters continues to increase. Among the causes are the large volumes of wastewater—often subject to little or no control—originating from highly populated cities, the discharge of untreated effluents by industrial complexes, and the use of a wide variety of chemical fertilizers and pesticides in agriculture. Its results include harm to humans and to animal and plant life, unpleasant odours, reduced water clarity, damage to property, and a reduction in the recreational quality of coastal and inland water and beaches.

Many people are willing to accept some environmental deterioration in exchange for a higher standard of living and a greater abundance of consumer goods but, as living standards rise, man-made water pollution is seen first as a major irritation and then as a threat to this very goal of an improved quality of life. Excessive pollution can jeopardize health, while certain types of pollution may even render some areas unfit for normal habitation and, therefore, constitute a serious obstacle to socioeconomic development. Hence many national, regional and city administrators are now faced with public demands for stricter control over water pollution.

All programmes to reduce pollution or to improve the quality of water used for human consumption depend on reliable analytical measurements. A large variety of analytical methods has been developed to determine important chemical and microbial determinands, and some biological survey methods have evolved to estimate the quality of surface water. Several of the analytical methods used in the assessment of pollution are not concerned with the concentration of specific substances but measure a general property of the water. These methods, of which the measurement of biochemical oxygen demand is an example, are empirical, but are carried out under carefully standardized conditions. The results obtained will depend on which conditions are employed for a given test. However, even when determinations are made of specific constituents, results may vary according to the particular analytical method used. It is therefore important to agree on a limited set of well-tested methods when undertaking any study that involves more than one analytical laboratory.

The number of published methods and variants of methods for any one determinand is often so large that different methods are apt to be used in different countries. In many countries there exists some form of agreement on the analytical methods to be employed in order that the results obtained in different laboratories may be comparable. Internationally, however, there are at present only limited agreements among countries, and strong opinion has been expressed that uniformity of analytical methods throughout the European Region is necessary.

Even when the same method is being used, the results from different laboratories do not always agree, and there is sometimes disagreement even between results obtained by workers in the same laboratory. In some places it is the practice to send out samples of known composition for analysis to laboratories to ascertain their levels of accuracy. This practice is valuable and could usefully be extended, both nationally and internationally.

Also, sampling is a vital link in the chain of information. Unless the sampling procedure is clearly defined, the analytical results can be misleading and a proper comparison of analytical data may not be possible. There are, sometimes among laboratories but more often among countries, differences in the terms in which results are expressed, and there is a need to promote uniformity in this matter also.

Although the WHO Regional Office for Europe had been implementing individual projects on water pollution for over 20 years, it was not until 1969 that, conscious of the seriousness of the problem, the WHO Regional Committee for Europe decided to adopt a comprehensive long-term programme on environmental health, including water quality and pollution control. The main aim of the programme was to develop management guides and decision aids for use by government administrations, executive agencies and scientific institutions concerned with the quality of the environment and the protection of public health.

Following the introduction of the long-term programme, a Working Group on Trends and Developments in Water Pollution Control in Europe was convened in Copenhagen in September 1969 to review the European situation. The recommendations of this Group formed the basis for programme activities in the water pollution sector. On the basis of its evaluation, the Group recommended that "a preliminary study should first be made comparing the analytical methods and the sampling procedures employed in water pollution control throughout the European Region. The project should culminate in the production of a European Manual of Methods of Analysis for Use in the Control of Water Pollution." Work began in 1970, when Professor V. Maděra was invited to undertake a limited comparative study of the more important analytical methods for the examination of water.

At the beginning of 1972, when the editor took over the responsibility for this project, a re-evaluation was made of its scope and purpose. It was soon recognized that a text of limited scope could not be justified, and the conclusion was reached that the involvement of the Regional Office in such a task could be justified only if three principles were accepted. First, the new text should cover the whole range of water analysis, starting with the planning of a sampling programme, sampling itself, evaluation of results, etc., and ending with the compilation of a laboratory manual. The aim was to provide a method for every analysis that might be required, including not only physical and chemical but also radiological, biological and microbiological examination. Second, it was felt that the average water laboratory in Europe, which is the first concern of the Regional Office, should be encouraged as far as possible to use a *single* method of analysis that had proved itself over the years to be reliable and workable, and which could be agreed on by experts from many countries in Europe and elsewhere. Third, once such an elaborate text had been completed, it could well serve as a standard work for the development of water sampling and analysis in any country in the world. Consequently, it was decided to enlarge the scope, and Professor Mancy and Dr. Suess prepared a detailed outline for consideration by a gathering of experts on water analysis and pollution control, which was convened specially for this purpose during the Sixth International Conference on Water Pollution Research, held in Jerusalem in June 1972. This group recognized the urgent need for such a comprehensive text and warmly endorsed the proposals for its new and enlarged structure.

The present 3-volume Handbook is the culmination of a decade of concerted effort by some 250 scientists from 31 countries in 5 continents (see Annex 1 of each volume). Eight scientific working groups, each addressing the subject matter of one or more chapters, met at various times to review the material and to recommend methods, terminology and additional requirements. Among the participants in these groups were representatives of four intergovernmental and five nongovernmental organizations. The working group meetings and their participants are listed in Annex 2 of each respective volume. Drafts underwent several reviews before and after the working group meetings, to ensure a reasonable uniformity of presentation and style.

The book is intended to provide information and recommendations which will assist in setting up water pollution control programmes and in establishing a unified system for analysing fresh and waste waters and recording the results. It is also designed to serve as a technical and laboratory guide for scientists, engineers and laboratory technicians active in the fields of water quality, pollution control and analysis.

The wide activities began in 1972, with emphasis on preparing a text that would not only concentrate on the presentation of standard methods but exhibit the unique feature of bringing together and treating all aspects of the entire process of water examination for pollution control, of which water analysis is just one.

When planning a water examination exercise, it is important to determine from the very beginning its objectives and, accordingly, develop an appropriate measurement programme. Often, water samples are taken without sufficient consideration of location, time and climate, and the sampling system within a whole catchment area is not always well coordinated. The need for and use of routine monitoring—be it automated or not—of specific determinands in the field and the advantages of automated techniques in the laboratory, imply strong cost–benefit characteristics in any modern water pollution control project. It is also useful to be well informed about recent developments in instrumental analysis, and their applications to water examination, even if such techniques are not essential for the routine work. The execution of any water pollution control and abatement programme at both the national and the international level is, from the scientific point of view, heavily based on the validity and availability of the data generated. To this end, it is important to understand the methods and to use proper techniques for the processing and storage of data for their retrieval when needed. Statistical treatment and error determination are essential for establishing the validity of data when these serve as a basis for decision making on technical, economic or political levels. Moreover, to ensure compatibility and comparability of data among different water laboratories, intercalibration and intercomparison exercises have to be developed and maintained.

Finally, not forgetting the human element involved, it is important to provide laboratory staff with properly structured premises. This includes well designed working spaces, correct placing of precious and sensitive instruments, adequate storage of materials, and appropriate service rooms and emergency facilities.

The first volume covers sampling, data analysis and laboratory equipment, and its seven chapters are the result of elaborate reviews and lengthy deliberations. The views and knowledge of water specialists from different professional disciplines were sought, considered, and generally amalgamated into the text, thus setting out the present international state of the art and a good projection of the needs for the future. It is hoped, therefore, that these chapters will provide water managers with a useful tool for their planning process and decision making.

The second and third volumes are solely and wholly devoted to the detailed description of analytical procedures. They provide concise and systematic descriptions of each method, including sampling, storage, standardization, precise operating instructions, and calculation of results for routine work, together with a single set of methods suitable for measuring all the determinands that may be important in the control of water pollution. In each case, an attempt has been made to describe the best method available for use in the average laboratory.

More specifically, the second volume deals with physical, chemical and radiological methods for the analysis of substances found in water. The methods have usually been classed as "reference" or "secondary", and these terms relate to the amount of experience available for a given method. A reference method is one that has been sufficiently well tested and proved to permit its unqualified recommendation, subject to any restrictions stated in the method itself. This is not to say, however, that the reference method is the most advanced or a highly instrumental one. When a reference method could not be identified, one or more secondary methods were selected. By implication, these are methods where, at present, WHO cannot provide an unconditional recommendation, either because of insufficient experience in its application or because doubts arise as to the accuracy of the results obtained. The latter class of method may, of course, be perfectly adequate for many purposes.

The method to be used for a particular determinand should be selected for its ability to provide the information required. This means, in particular, that the method should allow satisfactory levels of detection and accuracy to be achieved. When choosing a particular method, the presence of agents in the sample capable of causing interference must be recognized, and careful reading of instructions for analysis is therefore essential. When a method has been selected, the prescribed procedure should be closely followed, otherwise small changes of procedural detail may cause unexpectedly large errors. In applying these methods, the importance of proper control of any hazards (e.g. toxic chemicals, explosions, fires) cannot be overemphasized, and each laboratory should take all necessary precautions to ensure adequately safe working conditions. (Refer also to vol. 1, chapter 7.)

It is worth emphasizing that the use of these methods alone will not necessarily ensure accurate results. Many sources of error are usually present during sample collection and handling before analysis, and steps must be taken to control such errors (see vol. 1, chapter 2 and the relevant sections in individual methods). In addition, analytical errors have occasionally been found to be much larger than anticipated, even when standard methods were used. This is not surprising when one considers how many factors affecting accuracy cannot be controlled, even when the written description of the method is scrupulously followed. Accordingly, the provision of these methods does not in any way decrease the importance of each laboratory maintaining a continuously self-critical approach to the reliability of its results. As an aid to this, the techniques and tests for experimental estimation of accuracy, intercalibration and interlaboratory comparison exercises (see vol. 1, chapter 6) are strongly recommended as an integral part of the application of any analytical method.

An average laboratory could be expected to undertake routinely some radiological examination of water. In some countries, only one or just a few laboratories are assigned by the authorities to develop and maintain competence in the radiological examination of the environment, and they are then expected to possess the more sophisticated instrumentation and undertake the more complicated analyses. However, at least routine monitoring of gross radioactivity could and should be performed by the average water laboratory, even with relatively simple equipment and a properly trained laboratory technician. The more sophisticated analysis of individual nuclides and perhaps the interpretation of results should then be left to better-equipped laboratories and more highly qualified personnel.

The third volume deals with the sampling, identification and examination of organisms that may be found in water, from fish to viruses. Special attention is given to bacteriological assays, which are so important to the investigation of public health problems. Methods are presented for evaluating the quality of water based on an examination of the organisms living in it. Indices based on such analyses are capable of providing much information but have been relatively neglected in many countries.

The purpose of the chapter on virological examination is to encourage those working in the average water laboratory to become more aware of and interested in viruses, by providing them with some guidance and orientation, as well as some detailed concentration procedures. Hence, a collaboration can be envisaged between two types of laboratory, one being concerned with the sampling and concentration and the other—the more specialized—being responsible for the cultivation, enumeration and identification of the viruses. Under such circumstances transportation problems gain in importance, and the chapter deals with this subject too.

The list of references following each chapter reflects the completion date of that chapter. For this reason they are not completely up to date. However, the objective of this work was not to present the reader with a critical review of current literature. What is important is that the fundamental information contained in this publication is sound and will remain valid for many years. The only exception perhaps applies to the chapter on virological examination, a subject which at present is dynamic and in which new knowledge is accumulating rapidly. The updating of the material and references will be given consideration in a future revision.

By the very nature of works such as this, many subjects are handled in more than one place, and the reader is therefore encouraged to examine all three volumes. A great effort has been made to present a uniform text as regards style and terminology. Moreover, the general rule of the World Health Organization in its publications is to follow authoritative, internationally approved scientific terms and units, some of which are rather new. The reader is is therefore advised to study carefully the Note on Terminology which precedes this Introduction. While in general the mention of manufacturers' products and trade marks has been avoided, in a few cases it was necessary to use these in order to simplify the description of an analytical procedure. Such mention does not imply endorsement or recommendation in preference to others of a similar nature.

A number of sets of standard methods for the analysis of water and wastewater already exist and are in widespread use. Many of the methods in this book are based on one or more of these compilations, whereas others are based on later modifications, or on original methods reported in the literature, when no suitable standard method was available. Compilations of standard methods from various countries have all been reviewed in choosing the methods in vols. 2 and 3. Where the method is well established, liberal use has been made of these sources, which are widely used in European and other countries. The sources are as follows:

AMERICAN PUBLIC HEALTH ASSOCIATION, AMERICAN WATER WORKS ASSOCIATION & WATER POLLUTION CONTROL FEDERATION. Standard methods for the examination of water and wastewater, 13th & 14th ed., American Public Health Association, 1015 Eighteenth Street, NW, Washington, DC 20036, 1971 & 1976.

CANADA, INLAND WATERS DIRECTORATE, WATER QUALITY BRANCH. Analytical methods manual, Ottawa, 1974.

COUNCIL FOR MUTUAL ECONOMIC ASSISTANCE. Standard methods for water quality examination. Part I. Methods of chemical analysis of water, 2nd ed., Moscow, 1974.

GESELLSCHAFT DEUTSCHER CHEMIKER, FACHGRUPPE WASSERCHEMIE. Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung: physikalische, chemische und bakteriologische Verfahren, 3rd rev. ed., Weinheim, Verlag Chemie, 1975.

INTERNATIONAL BIOLOGICAL PROGRAMME (IBP) HANDBOOKS. Oxford, Blackwell Scientific Publications, 1969–1974.

UNITED KINGDOM, DEPARTMENT OF THE ENVIRONMENT. Analysis of raw, potable and waste waters, London, HM Stationery Office, 1972.

UNITED STATES, ENVIRONMENTAL PROTECTION AGENCY, METHODS DEVELOPMENT AND QUALITY ASSURANCE RESEARCH LABORATORY. Methods for chemical analysis of water and wastes, Washington DC, Office of Technology Transfer, 1974.

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In addition to its use for routine analysis at the national level, this Handbook has also been designed to serve international programmes such as interlaboratory calibration and comparative studies and transfrontier regional and river basin programmes. The United Nations Environment Programme (UNEP), the World Health Organization, The United Nations Educational, Scientific and Cultural Organization, and The World Meteorological Organization have already used parts of vol. 2 for the preparation of an operational guide for the cooperative water programme under the UNEP Global Environmental Monitoring System (known as GEMS).

Although the book was originally planned by WHO for use in European countries, in its present form it should be of equal value to countries all over the world, and to other international organizations which develop programmes aimed at the control of noxious effluents and the protection of natural water bodies. Moreover, it should provide water pollution control specialists everywhere with helpful information based on international practice.

The World Health Organization is grateful to the Governments of Austria, Belgium, Czechoslovakia, the Federal Republic of Germany and Hungary for their support in agreeing to host working group meetings, and to Belgium and the Federal Republic of Germany for special financial contributions which made the convening of some of the meetings possible.

Pergamon Press, the publishers of this work, are to be complimented for their cooperation in producing this scientific text in their best book publishing tradition.

I should like to record my personal indebtedness to all the colleagues, reviewers, and participants in the meetings who have contributed in many ways and at various stages. All of these are listed in Annex 1, acknowledging their contribution to the volume in question, and I offer my sincere apologies to anyone who may have been unintentionally excluded. The very close collaboration with the authors of the chapters and other particularly active contributors among the working group participants, many of whom have become personal friends in the course of the work, and their painstaking efforts to upgrade and update the material, are warmly acknowledged.

The friendly assistance and goodwill of various members of the Regional Office staff on different occasions is greatly appreciated. They include secretaries, draftsmen, publications and reproduction staff, registry and mailing personnel, and the administration. Though too numerous to mention individually, all have contributed toward the successful implementation of this project. I am also grateful to Mr J. Kumpf and Mr J. I. Waddington, former Chief and present Director, respectively, of the environmental health team in the Regional Office, for their continuous support during the implementation and completion of this mammoth work. Their far-sightedness and recognition of the potential value of this text in harmonizing water analysis methodology in many countries was a great