WATER ANALYSIS

VOLUME III

Organic Species

Edited by Roger A. Minear
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VOLUME III ORGANIC SPECIES

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Radian Corporation
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ACADEMIC PRESS, INC.
Orlando, Florida 32887

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Main entry under title:

Water analysis.

Includes bibliographies and index.
Contents: v. 1. Inorganic species, part 1 -- / -- v. 3. Organic species.
1. Water--Analysis. I. Minear, R. A. II. Keith, Lawrence H., Date .
QD142.W36 1982 628.1'61 82-1755
ISBN 0-12-498303-0 (v. 3)

PRINTED IN THE UNITED STATES OF AMERICA

84 85 86 87 9 8 7 6 5 4 3 2 1

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PREFACE

This is the final volume of this treatise. Whereas the first two volumes focused on inorganic constituents in water, this volume is centered around the organic constituents.

The first two chapters deal with waste strength and waste pollution parameters of a nonspecific variety. These include biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), spectroscopic measurements, electrochemical methods, and a number of other techniques that provide chemical class determinations.

The third chapter provides an in-depth review of the current methods available for isolating organic constituents from water and for concentrating and partitioning them. This is a critical step in the analytical procedure, and there are a multitude of techniques to choose from, each with advantages and disadvantages for different types of organic pollutants. A wrong decision at this point negates all of the following work because, no matter how accurate and precise the analysis is, if the sample is not representative, the data are in error.

Chapter 4 deals with gas chromatographic (GC) separations and analyses, one of the most popular and rapidly advancing techniques in the field of complex mixture analyses. Both capillary and packed-column techniques are discussed in depth in this well-illustrated chapter. In addition, injector techniques, derivatizations, detector types, qualitative and quantitative analyses, and a representative list of applications are presented.

Mass spectrometry (MS) is the method most often used to identify unknown organic compounds in environmental samples. Chapter 5 presents a comprehensive discussion on the principles of organic mass spectrometry, mass analysis, ion detection, chromatography/mass spectrometry, tandem mass spectrometry, qualitative and quantitative analysis, and selected applications.

Chapter 6 describes the principles and applications of using high performance liquid chromatography (HPLC) for water analyses. This is the most valuable technique available for separation and analysis of nonvolatile organic constituents from water. The necessary equipment, a description of the chromatographic process, and practical use and optimization of the method are presented in detail.

The final chapter covers the use of infrared (IR) spectrophotometry for analyzing for organic pollutants in water. Both theoretical considerations and practical applications of this technique are discussed in depth.

The chapters in this volume represent a collection of the state-of-the-art methodology in current use, which accounts for the major portion of the methods used for analysis of organic constituents in water. Together with the chapters on analysis of the inorganic constituents in water from the first two volumes, this treatise represents a comprehensive work on water analysis. Thus, we have attempted to provide, in a single source, a collection of detailed theoretical and applied treatments on each of the important methodologies necessary for understanding and determining the trace level components found in both natural and polluted waters.

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WASTE STRENGTH AND WATER POLLUTION PARAMETERS

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ISBN 0-12-498303-0

I. INTRODUCTION

Analysis of the organic content of wastewaters is essential to properly determine their treatability, to design water pollution control plants and monitor their performance, and to evaluate the impact of wastewater discharges on lakes and streams. The number and variety of compounds, their highly variable concentrations, the low concentrations of specific compounds, and the difficulty of identifying and measuring each compound have led to the general use of nonspecific or indirect tests to indicate the gross amount of organic material in water or wastewaters.

Biochemical oxygen demand (BOD) is perhaps the most widely used of these nonspecific tests. Basically, the BOD test measures the amount of oxygen used by microorganisms during aerobic decomposition of organic pollutants. The amount of oxygen used is an indirect measure of the amount of biodegradable organic material present in a given sample. Despite their importance, BOD tests and their results are poorly understood and widely misused.

The BOD test procedure is time consuming and may produce relatively imprecise results, and the interpretation of test data often is subjective. Because of these potential problems, nonbiological test procedures—for example, chemical oxygen demand (COD) and total organic carbon (TOC)—have been proposed as alternatives to the BOD test. These tests also provide nonspecific measures of organic content, but in terms of the chemical equivalent of the amount of oxygen required to oxidize the organic matter. Although these tests have the advantage of being more rapid and precise than the BOD test, they have the major disadvantage of not distinguishing between biodegradable and nonbiodegradable organic matter. BOD is the only parameter that provides an indication of the amount of biodegradable organic materials in wastewaters and in streams receiving wastewater discharges.

II. OXYGEN DEMAND AS A POLLUTION CONTROL PARAMETER

Oxygen demand was recognized in the late nineteenth century as being an important effect of the decomposition of organic material in natural waters. Samples of water from streams showed a definite depletion of oxygen if those streams received significant amounts of wastewater. As waste loads increased, the oxygen demand frequently caused the streams to become septic with resulting production of odors and occasional fish kills. Early attempts to quantify this effect involved placing samples of stream water in capped bottles and measuring the dissolved oxygen concentration (DO) over a period of time. Complete uptake of dissolved oxygen in 5 to 7 days indicated a significantly polluted stream while longer persistence of a DO residual signified acceptable stream conditions. Continued research on oxygen demand led to the formalization early in this century of the BOD test (Theriault, 1927; Phelps, 1944; Buswell *et al.*, 1954; O'Brien, 1962). Although research has continued, the currently recognized standard procedure was adopted in 1936, and few substantial changes have been made since that time.

The BOD reaction consists of two major phases as illustrated in Fig. 1. The first is a carbonaceous phase in which organic material is oxidized as shown by Eq. (1):

$$\text{Organic material} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + H_2O + \text{microbiological solids} \qquad (1)$$

The oxygen required for complete conversion of organic material to carbon dioxide and water is defined as the theoretical oxygen demand (THOD).

The accumulated first-stage oxygen consumption after a 20- to 30-day (theoretically infinite) period of incubation represents the ultimate BOD (BOD_u). Because some organic material remains as nonbiodegradable cell residue, it is not possible biologically to oxidize all the organic material

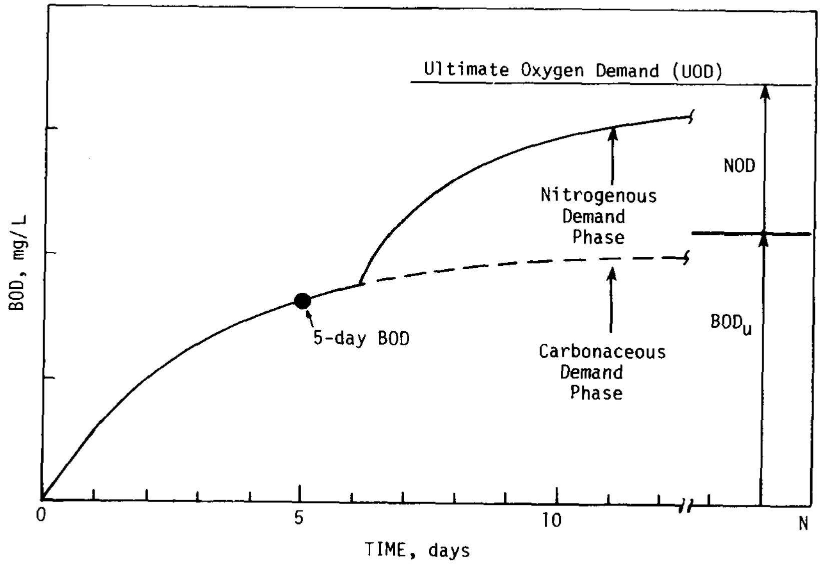

Fig. 1. Schematic representation of a typical BOD curve showing carbonaceous and nitrogenous BOD reactions.

originally present in a sample. Consequently, BOD_u is somewhat less than the THOD.

In the second phase, ammonia and nitrite are converted to nitrate as follows:

$$\begin{aligned}
&\text{a. } NH_3 + \tfrac{3}{2}\, O_2 \xrightarrow{\textit{Nitrosomonas}} HNO_2 + H_2O \\
&\text{b. } HNO_2 + \tfrac{1}{2}\, O_2 \xrightarrow{\textit{Nitrobacter}} HNO_3 \\
&\text{Net: } NH_3 + 2\, O_2 \xrightarrow{\qquad} HNO_3 + H_2O
\end{aligned} \tag{2}$$

These reactions collectively are defined as nitrification. Nitrifying organisms, especially *Nitrosomonas,* exhibit a lower maximum growth rate than the carbon-decomposing organisms, often causing nitrification to be delayed until much of the organic material has been oxidized. Both *Nitrosomonas* and *Nitrobacter* use carbon dioxide as their source of carbon for growth, and the nitrogenous compounds serve as electron acceptors. *Nitrosomonas* grow more slowly than *Nitrobacter* so that the conversion of ammonia to nitrite usually controls the rate of nitrification.

Theoretically, if the reactions in Eq. (2) are carried to completion, 3.43 g of molecular oxygen are used per gram of ammonia nitrogen oxidized to nitrite, and 1.14 g of oxygen are used for each gram of nitrite nitrogen converted to nitrate. However, some of the reduced nitrogen is assimilated as cell material by the nitrifying organisms, which reduces the amount of oxygen theoretically needed for nitrification. Although no means exists to determine the exact amounts of oxygen used in each of the above reactions, the following equation [Eq. (3)] predicts the nitrogenous oxygen demand (NOD) quite accurately (Wezernak and Gannon, 1968; Montgomery and Borne, 1966).

$$\text{NOD} = 3.22\,(NH_3\text{-N} \longrightarrow NO_2^-\text{-N}) + 1.1\,(NO_2^-\text{-N} \longrightarrow NO_3^-\text{-N}) \tag{3}$$

Therefore, if ammonia nitrogen exists in appreciable quantities, as it does in domestic and many industrial wastes, a significant part of the potential oxygen demand can be attributed to nitrification.

The BOD reaction is not as simple as Eqs. (1) and (2) imply but is a complex interaction between many species of microorganisms and a number of organic and nitrogen compounds. The initial stages of organic decomposition involve hydrolysis of high molecular weight sugars, proteins, fats, and starches, and synthesis of the products of these reactions. Other species of microorganisms grow in response to by-products released by these initial metabolic reactions. Eventually, predator organisms such as protozoa, amoebae, and stalked ciliates begin to graze on bacterial cells and other particulate organic material. Throughout these reactions, soluble organic by-products are released and become available to support further bacterial growth, and living microorganisms use oxygen for cell maintenance or endogenous respiration (Young and Clark, 1965; Bhatla and Gaudy, 1965; Gates and Ghosh, 1971).

A. Ultimate Oxygen Demand

When the total NOD is added to BOD_u, the result is known as the ultimate oxygen demand (UOD), or

$$UOD = BOD_u + NOD \tag{4}$$

The NOD can be calculated from Eq. (3) or measured by BOD test procedures. Although UOD has little utility in wastewater treatment, it can be used as a measure of the maximum oxygen-demanding load in wastewater streams discharged to receiving waters.

B. The 5-Day BOD

The oxygen uptake at 5 days of incubation and at a test temperature of 20°C is recognized in the United States and many other countries as the standard BOD. BOD_5 has become an important parameter for designing and evaluating the performance of water pollution control plants and for monitoring the quality of treated effluents. Response of receiving streams to oxygen-demanding waste loads commonly is determined from stream models using oxygen uptake rate and oxygen demand measurements as input parameters. The dependability of these models is closely related to the reliability of BOD_5 measurements (Dobbins, 1964). U.S. Public Law 92-500 (Water Pollution Control Act Amendments of 1972) and subsequent rules and regulations identified BOD_5 as one of the parameters to be used for establishing effluent and stream standards for point-source discharges. This means that the 5-day 20°C BOD takes on a legal meaning that originally was not considered in the test objective. Factors affecting the reliability and interpretation of BOD_5 measurements are discussed in the succeeding sections.

C. The Plateau

A plateau often is observed in the carbonaceous BOD reaction within 24 h of incubation (Fig. 2). The plateau generally represents the effect of a change between major phases of the carbonaceous metabolic reaction (Bhatla and Gaudy, 1965; Gates and Ghosh, 1971; Busch, 1958). The first phase involves the uptake of soluble organic substrate initially present in the sample; part is oxidized and part is synthesized into bacterial cell

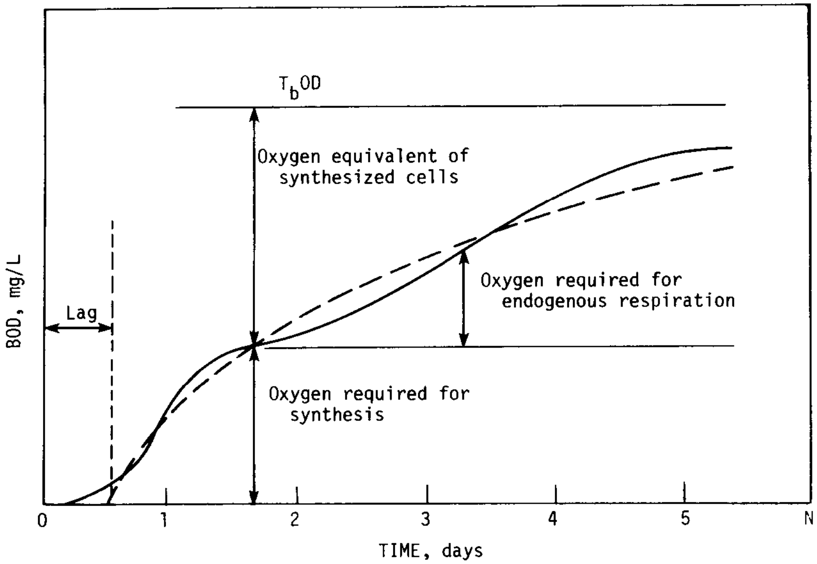

Fig. 2. Illustration of the occurrence of a plateau in the BOD reaction. The dashed line represents the first-order approximation of the reaction.

solids. The second phase is associated primarily with endogenous respiration of bacterial cells, growth of predator organisms that graze on bacterial cells produced during the first growth phase, lysis of microbial cells, and regrowth of bacteria on the soluble products released. A plateau also may be an environmentally induced artifact produced by chemical influences such as a pH change or by the release of organic by-products that temporarily inhibit bacterial growth or delay the onset of predator growth.

A plateau may not always be observed. Individual microbial reactions may be superimposed in such a manner that different metabolic phases are not distinguishable. Particulate organic matter is generally decomposed more slowly than soluble organics so that the BOD reaction for fresh raw domestic wastewaters may exhibit no plateau. Carbonaceous oxygen demand in samples of effluent from secondary or tertiary biological treatment plants is associated primarily with endogenous respiration. A plateau, therefore, is not expected to occur with samples of these wastewaters.

D. Lag

A lag occurs in the BOD reaction when an insufficient number of acclimated microorganisms is present (see Fig. 2). This lag can be reduced by adding seed microorganisms to the test sample. In some instances,