



Georgia Institute of Technology
STATE ENGINEERING EXPERIMENT STATION
Atlanta, Georgia

FINAL REPORT

PROJECT NO. 117

GRANT-IN-AID RG264C

RAPID CHEMICAL AND PHYSICAL ANALYTICAL TECHNIQUES
IN WATER AND SEWAGE ANALYSIS

Prepared for

NATIONAL INSTITUTES OF HEALTH
UNITED STATES PUBLIC HEALTH SERVICE

By

GEORGE W. REID
and
ROBERT S. INGOLS

OCTOBER 1, 1946--JANUARY 1, 1950

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I. SUMMARY

The research on rapid methods of water and sewage analysis supported by the National Institutes of Health has included investigations of individual techniques, comparison of time and equipment required for various techniques of analysis, and methods in general. Emphasis has been placed on micromethods, rapid semiquantitative procedures, and other time-saving modifications of existing techniques. Accomplishments include publications, six unpublished manuscripts, a 215-page literature search, and three specific recommendations to the Standard Methods Committees on modifications of techniques. Specific studies have been made of oxygen consumed, fluoride, magnesium, nitrogen, relative stability, hardness, chlorine, chromium, nitrate, and sulfate. Comparative studies have been made of B.O.D., O.C. and direct oxygen-demand measurements, dissolved oxygen, and cost of water and sewage analytical procedures.

II. INTRODUCTION

This project, supported by a grant-in-aid from the Surgeon General, U. S. Public Health Service, was initiated to study "Rapid Chemical and Physical Analytical Techniques in Water and Sewage Analysis."

The primary objective was the determination of the possibilities of using micromethods, rapid semiquantitative procedures, and physical methods of analysis in accomplishing the desired result.

In the solution of problems concerned with water and sewage analysis, attempts have been made to devise new and suitable analytical techniques and to modify such existing ones as are pertinent.

III. PERSONNEL

The project staff was as follows:

George W. Reid, Project Director, S.M. and Associate Professor of Sanitary Engineering.

R. S. Ingols, Chief Chemist, Ph.D. and Research Associate Professor of Sanitary Chemistry.

E. H. Shaw, Chemical Engineer, M.S. (resigned July 1, 1948).

P. E. Murray, Chemist, B.S. (resigned April 1, 1948).

J. C. Hildebrand, Chemist, B.S. (resigned September 1, 1949).

H. L. Lawless, Chemist, B.S. (resigned June 1, 1949).

R. W. Nippler, B.S., Chemist.

J. R. Munger, Laboratory Assistant.

C. E. Renn, Consultant.¹

L. C. MacMurray, Consultant.¹

IV. LABORATORY FACILITIES

The Georgia Institute of Technology has made available a special laboratory in which much of the developmental work on new procedures has been carried out. The laboratory contained practically all of the standard equipment found in analytical and physical laboratories. Among the special items which the school furnished the project is a Brown Recording Potentiometer and a 6 x 12 foot B. O. D. incubator room.

Other facilities of the Georgia Institute of Technology, including research instruments and machine shops, have been used regularly by the project. The machine shop fabricated a shaking machine for the Sierp apparatus, an electrode assembly for the physical-chemical measurement

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(1) Connected with the coordinate NIH project at Johns Hopkins University.

of dissolved oxygen, and several other special pieces of apparatus. The spectrophotometer of the School of Chemistry was employed in the fluoride ion studies.

V. EXPERIMENTAL WORK

A. Calcium Determination²

Calcium ion has been determined by a technique involving the use of urea to raise the pH of the solution containing both the calcium and oxalate ions, permitting the formation of large, readily filterable crystals of calcium oxalate. These are less contaminated by magnesium or aluminum oxalate, or excess oxalate due to the presence of the sulfate ion, than are the small crystals formed by the standard method. In addition, the over-all time for a set of duplicate determinations for calcium is reduced by the use of urea from 90 minutes to 40-50 minutes.

B. Oxygen Consumed Test²

The oxygen-consumed (O. C.) test was developed early and has been used regularly for other analytical studies, but no new developmental work on the procedure has been conducted recently. However, considerable data have been collected for the Standard Methods Committee of the Sewage Works Federation in order to permit evaluation of the technique for possible inclusion in the next issue of Standard Methods. The results obtained by the Cincinnati group of the Public Health Service indicate that the accuracy of the technique compares favorably with that of similar techniques developed at about the same time, but, because of the use of a smaller sample, it lacks the precision of the technique developed in Cincinnati.

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(2) Either published or to be published. See Tables I and II.

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In this rapid analytical procedure for determining chemically the amount of oxidizable material present in wastes, a small aliquot of sewage is added directly to a small volume of a one-to-one mixture of phosphoric and sulfuric acids containing some potassium dichromate, and the mixture is refluxed for 60 minutes in the presence of selenium.

TABLE I
PUBLISHED WORK

<u>Subject</u>	<u>Publication</u>
Oxygen Consumed	"An Oxygen Consumed Test for Sewage." <u>Water and Sewage Works</u> 95, 113 (1948).
Calcium	"Urea Hydrolysis for Precipitating Calcium Oxalate." <u>Analytical Chemistry</u> 21, 524 (1949).
Magnesium	"Water Analysis." <u>The Filter Press</u> 1949-1950, No. 4, 5 (1949).
Relative Stability	"A Study of BOD with Time as the Measurable Variable." <u>Sewage Works Journal</u> 21, 984 (1949).
General	"Rapid Analytical Techniques for Water and Sewage Analysis." <u>Public Works</u> 80, No. 1, 27 (1949).
General	"Measuring the Strength of Sewages and Trade-Wastes." <u>Water and Sewage Works</u> 97, 21, (1950).
Literature	<u>Bibliography on Water and Sewage Analysis.</u> Georgia Institute of Technology, State Engineering Experiment Station Special Report No. 28, Atlanta, 1948, 215 pp.

After oxidizing the sewage, the dichromate remaining is determined chemically. The oxygen-consumed value is calculated by the difference in the dichromate present before and after oxidation, and is corrected for the chloride concentration of the sample.

TABLE II

UNPUBLISHED WORK

Subject	Publication
Sulfate	"Sulfate Ion Determination with Bezidine Dihydrochloride" (Water & Sewage Works)* "A Volumetric Sulfate Ion Determination Using the Barium Ion and Versenate" (Analytical Chemistry)*
Nitrogen & Phosphorous	"Microkjeldahl Procedure in Water and Sewage Analysis"
Fluoride	"Determination of Fluoride Ion With Ferric Thiocyanate" (Analytical Chemistry)**
Chromium	"Notes on the Determination of Chromium with Diphenyl Carbozide" (Analytical Chemistry)*
Procedures	"Cost Study of Water and Sewage Analytical Techniques"
*Submitted for Publication.	
**Accepted for Publication.	

C. Fluoride Ion Determination²

The new ferric thiocyanate procedure, which has been accepted for publication by the editors of Analytical Chemistry, is rapid, and the color is stable. However, the technique is complicated by its sensitivity to the sulfate and hydroxyl ions. The ferric thiocyanate complex is decolorized by both the fluoride ion and the sulfate ion, with approximately 0.1 p.p.m. fluoride ion being equivalent to 20 p.p.m. of sulfate ions. In order to determine the extent of decolorization due to the fluoride ions, zirconyl ions are added and the ferric thiocyanate color is restored by an amount equivalent to the fluoride ion concentration. The zirconyl ion does not react with the sulfate ion.

From a re-examination of the original paper presenting the determination of fluoride with ferric thiocyanate it appeared that some study must be made of the effect of the sulfate ion on the ferric thiocyanate color complex. This work indicated that sulfate ions do change the color intensity of the ferric thiocyanate in the same manner as does the fluoride ion, but a concentration approximately 100 times that of sulfate ions is required for a similar change. However, this is the normal ratio of concentrations of sulfate ion to fluoride ion in natural water. Foster³ recommends that a small amount of ferric or thiocyanate ions be added to compensate for the color loss due to the sulfate ions, but, although the original color intensity is restored, the original sensitivity is lost. Thus, some other approach is needed. Because it is realized that the intensity of the ferric thiocyanate color is already known to be a function of pH, ferric ion concentration, thiocyanate ion concentration, and total ion concentration, it does not seem possible to compensate for a variable sulfate ion concentration. It has been found, however, that by the addition of a small amount of zirconyl ion to a second color tube containing the sample the ferric thiocyanate color intensity whose loss was caused by the fluoride ion, could be restored without changing the ferric sulfate complex or, conversely, the resultant ferric thiocyanate color complex.

The technique as presented requires two tubes containing samples, one with and one without zirconyl ions, and a third containing the reagents in distilled water. Stable colors are developed rapidly in

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(3) Foster, M. D. "Colorimetric Determination of Fluoride in Water Using Ferric Chloride." Ind. Engr. Chem. Anal. Ed. 5, 235 (1933).

the presence and absence of the fluoride ion, permitting immediate readings but it is then necessary to use a nomograph. From this discussion, it is evident that the procedure lacks the simplicity of the technique of Standard Methods. However, because no sulfate ion interference will be encountered, the ferric thiocyanate complex should be very useful for plants, adding the fluoride ion for control of dental caries. A small fluctuation in coagulant dosage would not produce an appreciable change in sensitivity of the ferric thiocyanate toward the fluoride ion. A manuscript is under preparation on the ratio of ferric to thiocyanate in the color complex.

D. Magnesium Ion Determination

Two rapid volumetric tests for total hardness have been published recently. One procedure, published in Russian literature, using trisodium phosphate has not been successful but the method of Schwarzenbach⁴ has proved very desirable. The Schwarzenbach technique employs a standard solution of the disodium salt of ethylenediaminetetraacetic acid (versenate) and a dye Erochromezwartz T (Nr241). Calcium and magnesium ions form soluble complexes with the versenate radical, and the dye changes color as the magnesium ion concentration is reduced below 10^{-5} M. The titration is rapid, accurate, and reproducible to one part in 100 above concentrations of 0.2×10^{-4} M. In order to determine the magnesium ion in a mixture containing the calcium ion, one ion must be removed or its concentration determined. The sample must be buffered to pH 9.8-10.0 during titration but this can be carried out with an ammonium hydroxide-ammonium chloride mixture. The titration is rapid and the end point is

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- (4) Schwarzenbach, G., Biederman, W., and Bangerter, F., "New, Simple Titration Method for Determining the Hardness of Water." Helv. Chim. Acta 29, 811 (1946).

sharp. In the presence of the magnesium ion the dye is wine red and in its absence, the dye is blue.⁵

E. Microkjeldahl Procedure²

A detailed procedure for use of a modified microtechnique for nitrogen analysis on sewage, water, slime, and sludge is being written, the accuracy of the technique being limited only by sampling. The procedure is simply the Hengar technique adapted to the needs of water and wastes.

F. Relative Stability Determination²

The possibilities of developing a short-time B.O.D. test in which time would be the measurable variable in the technique has been investigated. A combination of photoelectric cell and a recording potentiometer is used to measure the changes in color intensity of a sewage sample to which a redox potential indicator (methylene blue) has been added. The results obtained are unsatisfactory, apparently because of the excessive time consumed (lag period) during which the bacteria make the necessary changes in the redox potential of the sample and to the low initial redox potential of some of the samples which immediately decolorize the indicator.

At the request of the Standard Methods Committee of the Sewage Works Federation some further work on the relative stability test has been performed. The results indicate that the values obtained by the relative stability test are highly reproducible, but not accurate; this was indicated in the published manuscript. It is felt that, in spite of its

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- (5) Since the technique is published, it has been recommended to the Standard Methods Committee of the American Water Works Association, who were already considering the method.

inaccuracy as far as raw sewage is concerned, the technique should be left in Standard Methods as a means of analyzing the effluent of biologically treated sewage at small plants. Also, it has value in comparison to the B.O.D. so far as nitrification is concerned.

G. Amperometric Titration for Hardness and Chlorine

No further work has been done on hardness since the second annual report, but a careful comparison has been made of the amperometric technique of Haller and Listek⁶ against each of the volumetric techniques of Palin⁷ and Connell.⁸ The present O.T.A. test differentiates quite well between free and combined chlorine residuals at low chlorine values of 0.5 p.p.m. or less. However, it is frequently necessary to determine the nature of chlorine residuals in excess of 0.5 p.p.m. This can be done either in the amperometer titration procedure or with the volumetric methods of Palin and of Connell. It was found, however, that the amperometric procedure is time-consuming and that dichloramine is determined along with chlorine dioxide in the alkaline-treated sample. The necessity for four large portions for this procedure can also present difficulties in some research work.

The Connell technique serves reasonably well in differentiating between free chlorine and chloramine, but it does not indicate the type of chloramine that is present. The Palin technique differentiates between chlorine, trichloramine, dichloramine, and monochloramine, but it does not differentiate between chlorine and chlorine dioxide and is not

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- (6) Haller, J. F. and Listek, S. S., "Determination of Chlorine Dioxide and Other Active Chlorine Compounds in Water." Anal. Chem. 20, 639 (1948).
- (7) Palin, A. T., "The Estimation of Free Chlorine and Chloramine in Water." J. Inst. of Water Eng. 3, 100 (1949).
- (8) Connell, C. H., "Ortho-tolidine Titration Procedure for Measuring Chlorine Residuals." J.A.W.W.A. 39, 209 (1947).

accurate below 0.5 p.p.m. The Palin technique has been found by comparison to be so clear-cut in its differentiation of the types of chlorine compounds that further research has been initiated to determine the meaning of the titration values with organic amine compounds and to study the residual values required for cysticidal concentrations of Endamoeba hystilytica. Research reported at Harvard indicates that the differentiation into the various chloramine compounds by the Palin technique agrees with the spectrophotometric determination of the various compounds. On the basis of the study, a recommendation has been made to the Standard Methods Committee of the American Water Works Association that the Palin technique be considered for the next issue of Standard Methods.

It is believed that a minor variation in the present Palin technique will permit the procedure to differentiate between either chlorine or trichloramine and chlorine dioxide. At present no attempt is made to account for chlorine dioxide, but, by use of the technique of Haller and Listek, a second aliquot can be treated with alkali to pH 12 while the first aliquot is run through the Palin procedure. After the second aliquot has been neutralized, the Palin procedure can be repeated; the alkaline treatment will leave the chlorine unchanged while the chlorine dioxide will be destroyed, and trichloramine will be changed to monochloramine. Thus, it is possible to differentiate between chlorine and chlorine dioxide or chlorine dioxide and trichloramine, but this suggested modification is not advised for differentiation between chlorine and trichloramine. The extraction of the trichloramine with carbon tetrachloride is still desirable.

H. Chromium Determination²

A hypothesis is advanced that chromate is adsorbed on the glass of the oxidation or digestion flask. The amount adsorbed becomes appreciable in samples containing less than 0.1 mg. chromium per 50 ml. sample (2.0 p. p. m. chromium). This adsorption is reduced by the use of new flasks. Adsorption is more pronounced from an acid medium; therefore, the alkaline digestion gives better recovery of small amounts of chromium.

The addition of cobalt ion is suggested for the more rapid breakdown of the excess hydrogen or sodium peroxide in an alkaline digestion procedure.

I. Nitrate Determination with Brucine

At present, nitrates may be determined by phenoldisulphonic acid or by reduction followed by Nesslerization. Either test is slow, but the phenoldisulfonic acid test color is extremely stable and the ammonia of the reduced test may be run in connection with other ammonia analyses.

However, the brucine sulfate test is rapid and simple except that its color is not stable indefinitely and the brucine sulfate reagent must be renewed at regular intervals. Although generally the size of sample is no problem, in water analyses the brucine test operates on a very small aliquot (5 ml.). For samples having more than 10-12 p.p.m. nitrate, a smaller aliquot is recommended for better accuracy and reproducibility. Checks on the interference of various ions and organic material indicate that these should not interfere with the accuracy of the results at the concentrations normally found in sewage.

J. Sulfate Ion Determination with Benzidine²

The standard methods technique for sulfate ion has been improved by refinements in precipitation by controlled cooling. Two discs of filter paper (Whatman 542, 2, 1 cm. dia.) in a Gooch crucible are used for filtration and ice is used for cooling.

K. Sulfate Ion Determination with Versenate and Barium Chloride²

The "Versenate test" for total hardness, as described by Schwarzenbach, consists of titrating the calcium and magnesium ions with the disodium salt of ethylenediaminetetraacetic acid (Versenate). The sample is buffered to a pH of 10 and the indicator used is Eriochromeschwartz T, (F-241). The end point consists of a change from wine red to blue. The calculation of the total hardness is made by multiplying the number of ml. of the versenate by a factor dependent upon the strength of the standard and the size of the sample.

This technique incorporates the above method with additions in order to determine the sulfate ion concentrations generally found in water. It can be modified to determine them in any concentration. The value of this technique lies in its speed and accuracy.

The principle of the technique is the removal of the sulfate ion with a known amount of standard barium chloride solution and the titration of the excess barium chloride with versenate, using Eriochromeschwartz T indicator. From this, the amount of sulfate can be computed with a high degree of accuracy.

L. B.O.D. Studies²

A comparison of the B.O.D.'s of raw and blended sewage to the theoretical B.O.D. and the C.O.D. values indicates the advisability of ob-

taining C.O.D. values along with the B.O.D. to provide a better understanding of the strength of sewage. No greater degree of definite formulation can be offered at this time.

M. Direct B.O.D. Studies

A modified Seirp apparatus for studying the rate of the B.O.D. reaction by following the dissolved oxygen directly with the dropping mercury electrode has not been successful. Some time has been spent in the development of the apparatus, but the test results were good only up to 48 hours. Dr. Morris, Harvard, according to personal correspondence, experienced a similar toxicity of mercury to sewage after an incubation period of 48 hours.

N. Electrometric Techniques for Dissolved Oxygen

A technique has been developed by Olson⁹ and co-workers for determining dissolved oxygen by the use of an electrode system consisting of a small platinum wire and calomel half-cell, with an electrical device that alters the polarity and measures the current from the depolarizing materials present. The technique was developed to study the B.O.D. of sewage, but calibration curves with sewage indicate that the electrode system does not function in sewage. It was found that sewage interferes with the decrease in current which is obtained with decreasing oxygen tension. Thus, the zero dissolved-oxygen curve is superimposed on the air-saturated oxygen curve in sewage. Some material in sewage is capable of depolarizing the platinum electrode (in the absence of oxygen) to the same extent as does oxygen in pure water.

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(9) Olson, R. A., Brackett, F. S., and Crickard, R. G., "Oxygen Tension Measurement by a Method of Time Selection Using the Static Platinum Electrode with Alternating Potential." J. of Gen. Phys. 32, 681 (1949).

If the material which depolarizes the platinum consists of a large molecule, then it is possible that the use of a film over the platinum electrode might help the situation. For this, it must be assumed that the film is permeable to oxygen and impermeable to the other depolarizing material. Two films were studied: agar and collodion. The agar film provides a satisfactory electrical covering, but it is very poor mechanically and seldom works adequately. As might be expected, the use of a film gives a slow rate of reaction to the change in dissolved oxygen. The collodion gives better mechanical properties but poorer electrical responses to changes in the dissolved oxygen level. Neither protective film gives values which indicate that extended B.O.D. work with sewage would be possible.

O. Cost Study of Water and Sewage Analytical Procedures and Resulting Equipment²

An attempt has been made to group various analytical procedures according to the principal method of analysis used and to evaluate the relative times required by the two groups of procedures. One of the NIH projects has indicated a very rapid system of analysis using expensive instruments. The work of this project has shown that volumetric and colorimetric procedures can give most of the essential chemical information for water in a short time without expensive instruments. A brief review of the essential analyses that must be performed by small water or sewage treatment plants will be developed, the purpose being to give a general outline of the laboratory facilities that should be maintained for proper control of water and sewage. Proper control will, of necessity, be a balance between the control desired by the regulatory authorities and the most economical control which the plants can give

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while maintaining a reasonable picture of operations. Obviously, control will be scaled to the size and location of plants.

The scheme of tests to be recommended will include the simplest techniques, so that they are economical from the standpoints of both equipment and personnel required. Recommendations will be developed for the size, location, and facilities required for the laboratory.

P. Literature Search²

The Bibliography on Water and Sewage Analysis¹⁰ constitutes an indexed guide to the pertinent literature on water and sewage analysis, prepared so that future work might benefit through use of and acquaintance with existing data. References have been classified according to subject under "tests" for various materials and properties. Access to references on "methods of analysis" and related subjects has been made possible by lists of pertinent reference numbers. References are numbered consecutively throughout the book, and all items include bibliographic reference to abstracts where these are known to exist. An author index is included.

VI. FUTURE WORK

Much of the work on the project is in the final stage. This work on specific techniques and on a general system will be completed at the expense of the Georgia Institute of Technology. At the completion of

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- (10) Weil, B. H., Murray, Poagie E., Reid, George W., and Ingols, Robert S., Georgia Institute of Technology, State Engineering Experiment Station Special Report No. 28, Atlanta, 1948, 215 pp.

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the program, a covering manuscript will be forwarded to the National Institutes of Health.

Respectfully submitted:

Geórge W. Reid,
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