GEORGIA INSTITUTE OF TECHNOLOGY

Engineering Experiment Station

PROJECT INITIATION

Date: ~~June 27, 1972~~

Project Title: Wastewater Sampling and Testing Instrumentation

Project No.: A-1439

Project Director: Dr. T. F. Craft

Sponsor: Air Force Special Weapons Center, Kirtland AFB

Effective . . . June 12, 1972 . . . . Estimated to run until: . . March 12, 1973 * . . . .

Type Agreement: Contract No: F29601-72-C-0149 . . . . Amount: $ 46,958 ** . . .

* Plus 2 months for final reporting effort

** Incrementally funded at $5,000 through June 30, 1972

REPORTS REQUIRED: R & D Contract Status Reports
Alternate Management Summary Reports
Final Technical Report

CONTACT PERSONS:

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Mr. R. J. Whitcomb	Air Force Weapons Lab. (DEE-W)
ONR Resident Representative	Kirtland Air Force Base, N. M. 82117
Hinman Research Building	
Georgia Institute of Technology	
Atlanta, Georgia 30332	

Assigned to . . Nuclear & Biological Sciences . . . . . . Division

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RA-62

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

A-1439 -2

PROJECT TERMINATION

Date June 14, 1973

PROJECT TITLE: Wastewater Sampling and Testing Instrumentation

PROJECT NO: A-1439

PROJECT DIRECTOR: Dr. T. F. Craft

SPONSOR: Air Force Special Weapons Center, Kirtland AFB

TERMINATION EFFECTIVE: May 10, 1973

CHARGES SHOULD CLEAR ACCOUNTING BY: June 30, 1973

Final Report Mailed 5/10/73

Remaining Contract Actions: Final Patent Report
Closing Documents & Final Voucher

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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

July 18, 1972

Air Force Special Weapons Center
Kirtland Air Force Base
New Mexico 87115

Attn: Capt. D. D. Nelson, Technical Monitor

Subject: Contract No. F 29601-72-C-0149, Ga. Tech No. A-1439
First Monthly R&D Contract Status Report, 13 June-12 July, 1972.

Trade journals and other publications have been searched for the names and addresses for companies who might supply wastewater monitoring instruments suitable for Air Force use. So far 235 possible suppliers have been located, and a form letter (copy attached) sent to each.

About 50 written replies have been received. Approximately half of these concerned instruments or devices that are potentially acceptable and will require consideration. The other half have nothing to offer. Several telephone calls have been received and two representatives have called in person. Requests for customer's names and addresses have been to six manufacturers, but insufficient time has passed to receive any replies.

Copies of the questionnaire and covering letter which will be sent to users are attached. We will enclose a stamped, self-addressed envelope with each questionnaire in ~~order to~~ make response as great as possible.

In the search for suppliers approximately 25 company names, without addresses, were found. Requests for addresses have been sent to the editor of the publication in which the names appeared.

During the next month it is expected that the flow of responses will diminish and it will be necessary to begin to follow up with those companies that have not replied.

Yours truly,

T. F. Craft,
Senior Research Scientist

Addressee: 2 copies
Mr. Steve Jorgenson: 1 copy

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

Gentlemen:

As consultants to the United States Air Force, we are to recommend for purchase wastewater sampling and testing instrumentation for use in monitoring influents and effluents at Air Force base waste treatment plants and from specific industrial operations. We are, therefore, searching the commercial market for equipment and devices that are most suitable for the particular needs of the Air Force. The main items of interest are listed on the attached sheet, but this is not intended to exclude any additional factors that may be pertinent.

Automated on-line instrumentation will be preferred, but for parameters that cannot be determined in this manner, other automated or semi-automated procedures will be utilized. If you market equipment that you would like to have considered, please send information including specifications, cost, availability of replacement parts, anticipated maintenance schedules, and any other factors that would assist in evaluation of your product. Duplicate copies of printed material would be helpful.

The time allotted to the collection of information is limited, and a reply at your early convenience would be appreciated.

Yours truly,

T. F. Craft
Senior Research Scientist

TFC:lsg
Enclosure

Items of particular importance in wastewater at United States Air Force installations:

Hydraulic Loading	Turbidity
Color	pH
Temperature	Dissolved Oxygen
Filterable Solids	Dissolved Solids
Organic Loading (TOC, COD, etc.)	Residual Chlorine
Total Cyanide	Total Oils & Grease
Mercury	Free Oils & Grease
Silver	Cadmium
Copper	Lead
Nickel	Zinc
Iron	Total Chrome
Phenol	Hexa-valent Chrome
Surfactants	Total Phosphates
Nitrates	Organic Phosphates
Nitrites	Total Nitrogen
Conductivity	Flow Meters
Sampling Devices	

Instruments capable of sensing more than one parameter

Georgia Tech Survey of Wastewater Monitoring Instrumentation

Name:

Individual answering questions: Title or position:

Type of wastewater treated: Domestic___ Industrial___ Combined___

How many years of experience have you had in the wastewater field?

Instrument: Manufacturer:

How many of these instruments do you have in your plant?

How long have they been in operation? Estimated total useful life: ____yrs.

Do you consider the instrument satisfactory? Yes___ No___ Partially___

Is it sufficiently accurate for your requirements? Is it reliable?

How frequently is calibration necessary?

Is it simple to operate? Is scale or meter easily read?

Are knobs or controls (if any) readily accessible? Too accessible?

What are the undesirable features of the instrument?

Is there anything in your normal operation that causes any interference with the instrument?

How often do you routinely service it? Is it difficult to service?

How often does it break down?

Can you (or someone in your plant) repair it? Is repair difficult?

How much time does it take? Are spare parts readily available?

Is outside help necessary for repair?

About how long does it take to get outside help?

Do you have instruments of any other brand for the same purpose as this one?

Manufacturer: Which do you prefer?

Why?

If you were building a new plant, which brand would you buy?

Any comments would be welcome - write on the back of this page or a separate sheet.

Your cooperation is greatly appreciated!

ENGINEERING EXPERIMENT STATION

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA 30332

As consultants to the United States Air Force, we are seeking information on instruments for wastewater sampling and monitoring that are suitable for Air Force requirements. It is believed that the most reliable information will come from those who have had personal experience with the instrument for a significant length of time.

The manufacturer of the instrument noted on the enclosed sheet has given us your name, and it would be greatly appreciated if you will share with us your experience with this equipment. A self-addressed stamped envelope is enclosed for easy return of the completed questionnaire. Your response will be held in confidence, and will not be individually revealed. We solicit your cooperation and look forward to hearing from you in the near future.

Yours truly,

T. F. Craft, Ph.D.
Senior Research Scientist

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

August 15, 1972

Air Force Special Weapons Center
Kirtland Air Force Base
New Mexico 87115

Attn: Capt. D. D. Nelson, Technical Monitor

Subject: Contract No. F 29601-72-C-0149, Ga. Tech No. A-1439
Second Monthly R&D Contract Status Report, 13 July-12 August, 1972.

Our initial letter of inquiry sent to 235 potential instrument suppliers has now brought approximately 125 responses. Follow-up letters with the hand-written note "Second Request--Do you have anything to offer?" are being mailed to those who have not yet responded.

Many of the replies indicate the availability of instruments or equipment that needs to be considered for Air Force use. Each of these companies has been asked to supply the names of users, and about ten such lists have been received. A few manufacturers have not revealed any user names stating that they sell only through agents and do not have this information. Another reported that they don't keep any records of customers and one indignant refusal voiced the suspicion that the information would be used to their detriment.

Questionnaires have been mailed to a total of about 200 users, and about 50 replies have been received. Most of the questionnaires returned are filled out in very ~~good~~ order, and a number include comments which we regard as very significant.

Contact has been established by letter or telephone with the few major suppliers of multi-sensing units, and considerable effort will be devoted to evaluating the performance of these systems.

Yours truly,

T. F. Craft,
Senior Research Scientist

Addressee: 2 copies
Mr. Steve Jorgenson: 1 copy

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332
September 15, 1972

Air Force Special Weapons Center
Kirtland Air Foce Base
New Mexico 87115

Attn: Capt. D. D. Nelson, Technical Monitor

Subject: Contract No. F 29601-72-C-0149, Ga.Tech No. A-1439
Third Monthly R&D Contract Status Report, 13 August-12 September,1972

Follow-up letters sent to potential instrument suppliers have now raised the total responses to approximately 195 out of a total list of 235. It appears unlikely that the remaining 40 have anything significant to offer.

Most of the manufacturers have been very cooperative in supplying customer names, although a few have declined, and no answers have been received as yet from several others. In at least one case, and I suspect others, the manufacturer has written to his customers and asked if they would be willing to participate. It has not been determined if this will change the percentage of responses.

To date about 450 questionnaires have been sent to customers of 23 different companies, and about 55% have been returned. Most questionnaires returned contain sufficient information to be useful, and many of them contain detailed comments. Several have been accompanied by lengthy letters containing much valuable information. Many respondents express considerably less than complete satisfaction with specific instruments, and it is believed that we are obtaining representative opinions.

Yours truly,

T. F. Cratt,
Senior Research Scientist

Addressee: 2 copies
Mr. Steve Jorgenson: 1 copy

ENGINEERING EXPERIMENT STATION

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

October 24, 1972

Air Force Special Weapons Center
AFWL/DEE-W
Kirtland Air Force Base, New Mexico 87115

Attn: Captain D. D. Nelson, Technical Monitor

Subject: Contract F 29601-72-C-0149, Georgia Tech A-1439
Fourth Monthly R&D Contract Status Report,
13 September-12 October, 1972

During the month, conferences were held at Kirtland Air Force Base and at Atlanta. Comments and suggestions received on both occasions will be helpful in achieving the goals of this contract. It is our intention to fulfill completely the requirements of the Air Force, and any additional assistance will be welcome.

Dr. R. S. Ingols visited the Environmental Protection Agency, Cincinnati, Ohio, and conferred with individuals knowledgeable in wastewater instrumentation. This very satisfactory visit elicited useful information, and we were assured of their full cooperation in our efforts.

The WPCF Annual Conference in Atlanta was of great assistance, as it was possible to meet with representatives of a large number of instrument manufactures in a brief period of time. The personal contacts seemingly will have a beneficial effect, as two long-delayed answers have already been forthcoming.

A TOD Analyzer will be loaned to us for testing by Ionics, Incorporated. Loan of other instruments was also requested at the Conference, and answers should be received shortly.

Yours truly,

T. F. Craft
Senior Research Scientist

Addressee: 2 copies
Mr. Steve Jorgenson: 1 copy

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332
November 28, 1972

Air Force Special Weapons Center
AFWL/DEE-W
Kirtland Air Foce Base, New Mexico 87115

Attn: Captain D. D. Nelson, Technical Monitor

Subject: Contract F 29601-72-C-0149, Georgia Tech A-1439
Fifth Monthly R&D Contract Status Report,
13 October-12 November, 1972

Follow-up letters have been sent to these instrument manufacturers who have not furnished satisfactory lists of instrument users. A number of lists have been received that were out of date, contained non-specific addresses, or were otherwise inadequate. It is felt that these responses indicate a lack of interest, but efforts will continue to obtain the needed information.

User responses continue to be received, although at a reduced rate. Many responses include detailed discussions and comments that are regarded as very significant. The response rate continues at slightly more than half the inquiries sent.

A TOD analyzer has been loaned to us for evaluation by Ionics, Inc., and will be installed at a local water pollution control facility within the next few days.

Yours truly,

T. F. Cráft
Senior Research Scientist

TFC/mw

Addressee: 2 copies
Mr. Steve Jorgenson: 1 copy

ENGINEERING EXPERIMENT STATION

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA 30332

December 14, 1972

Air Force Special Weapons Center
AFWL/DEE-W
Kirtland Air Force Base, New Mexico 87115

Attn: Captain D. D. Nelson, Technical Monitor

Subject: Contract F 29601-72-C-0149, Georgia Tech A-1439
Sixth Monthly R&D Contract Status Report,
13 November-12 December, 1972

We have sent follow-up letters and made telephone calls to manufacturers of instruments that have not previously responded to our requests. As a result, additional useful information has been received. Completed questionnaires continue to come in, but at a reduced rate; as previously noted.

A TOD Analyzer has been loaned to us by Ionics, Inc. and a company representative spent a day and a half with us starting up the device. The instrument will be used continuously at the Flint River Plant of the City of Atlanta. The initial sampling point is on the influent line to the activated sludge basins. Some difficulty is anticipated with respect to suspended matter, but a glass wool filter is being used and troubles have not materialized so far. Other sampling points will be utilized later.

Biospherics, Inc. is lending us a suspended solids meter, and it should be enroute to us at the present time. It will also be installed at the Flint River Plant.

Yours truly,

T. F. Craft, Ph.D.
Senior Research Scientist

TFC/mw

Addressee: 2 copies
Mr. Steve Jorgenson: 1 copy

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

January 18, 1973

Air Force Special Weapons Center
AFWL/DEE-W
Kirtland Air Force Base, New Mexico 87115

Attn: Captain D. D. Nelson, Technical Monitor

Subject: Contract F 29601-72-C-0149, Georgia Tech A-1439
Seventh Monthly R&D Contract Status Report,
13 December, 1972-12 January, 1973

Correspondence concerning instruments has been at a low level during the past month due to year end holidays here and elsewhere. Some replies are still being received, but little additional significant information is expected.

Testing of the TOD Analyzer loaned to us by Ionics, Inc. has continued. We previously reported no difficulty with suspended matter, but this situation has been reversed. Solid matter has a very adverse effect, stopping up the sampling line at unpredictable intervals. It is believed that regular observations and good maintenance practices would eliminate this problem. So far we have been unable to correlate TOD readings with BOD values, but we expect to run additional BOD tests to ascertain what correlation, if any, exists.

The suspended solids meter promised to us by Biospherics in mid December has not yet been received. A definite delivery date has been promised the week of January 15.

Yours truly,

T. F. Craft, Ph.D.
Senior Research Scientist

TFC/mw

Addressee: 2 copies
Mr. Steve Jorgenson: 1 copy

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

February 23, 1973

Air Force Special Weapons Center
AFWL-DEE-W
Kirtland Air Force Base, New Mexico 87115

Attn: Captain D. D. Nelson, Technical Monitor

Subject: Contract F 29601-72-C-0149, Georgia Tech A-1439
Eighth Monthly R&D Contract Status Report,
13 January, 1973-12 February, 1973

During this period, testing of the Ionics, Inc. Total Oxygen Demand Analyzer has been continued. Considerable difficulty has been encountered in maintaining a continuous flow of process liquid to the instrument. This is due mainly to the high suspended solids content of the liquid. Additional difficulties developed later and required considerable time plus consultation with the factory representative before they were eliminated. It is now obvious that this device is too complex to recommend for use except under the immediate supervision of a highly trained individual.

A visit to Orion Research, Cambridge, Mass. was made by T. F. Craft. Much useful information on specific ion electrodes was obtained and will be included in the final report. Orion has since loaned us a Fluoride Monitor for test purposes. Although fluoride per se is not of particular interest, it allows an evaluation of the monitor system by measuring a variable characteristic of the effluent from the Flint River Plant. So far, the instrument has functioned very well.

The suspended solids meter promised us by Biospherics has still not yet been received. The latest information indicated arrival in late February. Another suspended solids meter manufactured by Nuclarus Limited, Toronto has come to our attention, and a demonstration will be held on February 28. The device will be left here for some additional testing.

The final report is now being written, and should be completed on schedule.

Yours truly,

T. F. Craft, Ph.D.
Senior Research Scientist

TFC/mw

Addressee: 2 copies
Mr. Steve Jorgenson: 1 copy

WASTEWATER SAMPLING AND TESTING INSTRUMENTATION

by

T. F. Craft and R. S. Ingols
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

Contract No. F 29601-72-C-0149
EES No. A-1439
March, 1973

ABSTRACT

Liquid wastes produced at Air Force bases require monitoring of their characteristics to ensure disposal in a nonpolluting manner. A market survey of commercially available wastewater sampling and monitoring equipment has been made. Information was gathered from vendors and directly from users by a questionnaire. A total oxygen demand analyzer, a fluoride monitor, and a dissolved oxygen analyzer/controller were field tested. Continuous on-line equipment of proven reliability was located and recommended for measuring conductivity, dissolved oxygen, hydraulic loading, ORP, pH, residual chlorine, temperature, and turbidity. Less acceptable continuous, automatic, or semi-automatic devices for measurement of a large number of parameters were found, but are recommended only where manual procedures are not feasible. For some additional measurements only manually performed laboratory methods are available. Various types of samplers are discussed and recommendations are given. It is concluded that the field of instrument development is very active, and a continuing surveillance of the market is recommended.

CONTENTS

ILLUSTRATIONS

TABLE

SECTION I

INTRODUCTION

Water pollution is a widely recognized problem of national interest and concern. Production of pollutants parallels the growth of population and industry, and pollution control activities must be intensified to overcome the growing problem. The United States Air Force, recognizing the need for effective water pollution control, is taking action to become a leader in this area.

Typical municipal and industrial wastewater may vary rapidly in both quality and quantity, and astute management of disposal procedures requires a continuous monitoring of the waste stream. It is important for a treatment plant operator to know the character of the waste to be treated so that operating conditions may be optimized. Information concerning the treated flow is vital, as it reveals not only the results of treatment processes, but also the suitability of the effluent for release to the environment.

All Air Force bases produce liquid wastes that require disposal in a manner that does not violate state or federal regulations for the discharge of pollutants into public waters. These wastes may be of industrial and domestic types which may be treated separately or combined. In some instances, these waste effluents may be released for treatment in local community facilities. But whether a waste is treated on-site or elsewhere, information on its pollutional characteristics is needed.

Successful measurement of these characteristics frequently proves to be much more difficult than might appear to those without experience in the field. In general, problems may be due to human error in selecting, calibrating, reading, or servicing of instruments. Other sources of difficulty are instrument failures due to electronic or mechanical causes.

No analysis can be any more reliable than the sample on which it is performed, and obtaining a suitable, representative sample is, therefore, a critical matter.

Initially, any instrument should be chosen with careful regard to its intended purpose, and the most accurate instrument is not necessarily the best. For instance, it would be inappropriate to measure temperature to the hundredth of a degree when accuracy within half a degree is entirely satisfactory for normal waste treatment situations. In contrast, the concentration of pollutants such as the heavy metals needs to be determined with a very high degree of accuracy. When a limiting value of, say 1.0 milligram per liter (mg/ℓ) has been established, the analytical procedure should provide an uncertainty not greater than 0.1 mg/ℓ and preferably less.

In measuring elements present at low concentrations it is necessary to consider the magnitude of statistical fluctuations as well as the sensitivity of the instrument. Statistics are a matter of considerable importance in instances where the strength of a signal produced by an instrument is comparable in magnitude to the background noise level of the instrument.

Other instrumentation difficulties arise from the nature of the system being measured. For example, pH meters tend to drift when used in waters of low buffer capacity. Similarly, conductance measurements are poor when the ion content of a solution is low.

Interferences are common in many analytical procedures, and precautions are required to overcome them. In wastewater examinations, color may interfere with turbidity measurement and vice versa. Turbidity measurements may also be strongly influenced by particle size of the suspended matter. The presence of matter that is only slowly biodegradable produces a biased estimate of the actual pollutional potential of a waste. In analyses involving an organic reagent that produces color in the presence of a particular ion, elaborate separation techniques are frequently required to avoid interferences from other ions.

In spite of all these possible sources of error and difficulty, most problems arise from mechanical causes. Typically a pump supplying the sampling line may fail, tubes become plugged, or a sensing membrane becomes coated. Many of these difficulties can be avoided through attentive maintenance, but no reasonable program of inspection and maintenance can eliminate them entirely.

A great many devices are commercially available for sampling and measuring many of the parameters of pollution and it is often difficult to select the best instrument for a specific purpose. A comparative evaluation has been made and is presented here to assist in making a rational choice of available instruments to meet the particular needs of the Air Force.

SECTION II

MARKET SURVEY

TECHNIQUE

The initial activity consisted of locating suppliers of instruments that might be suitable for Air Force use. Numerous directories were consulted and advertisements appearing in recent issues of appropriate scientific and trade journals were carefully examined. A master list was prepared which included the names and addresses of all companies that appeared even remotely likely to have useful devices. Additional names were obtained from miscellaneous sources and during attendance at the equipment show which was part of the Water Pollution Control Federal National Conference held in Atlanta, October 8-13, 1972. Manufacturers, sales representatives, and resellers were all included on the list which ultimately totaled 264 names. Figures 1 and 2 illustrate a form letter and list of parameters of interest that was mailed to each company. The letters were addressed individually, and each carried a personal signature in blue ink. Responses by mail, telephone, and personal visits commenced a few days later. A great deal of information was received, examined, and evaluated.

Each company which offered instruments appearing useful was asked to furnish the names and addresses of 10 to 25 users of their instrument that could be contacted for their experience. It was requested that the names of specific individuals be given where possible. Company responses to this type of request were generally quite good, although a few declined to furnish this information on the basis of company policy or other nebulous reason. In a number of instances, company interest appeared genuinely high, but the instrument was so new that few, if any, were in routine use. Consequently, some customer lists consisted of only one or two names. Other lists included far more names than requested, but this allowed a wide choice of geographical locations and type of industry involved.

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

March 1, 1973

(SAMPLE)

XYZ Instrument Company
116 Ridley Circle
Decatur, Georgia 30030

Attn: Sales Manager

Gentlemen:

As consultants to the United States Air Force, we are to recommend for purchase wastewater sampling and testing instrumentation for use in monitoring influents and effluents at Air Force base waste treatment plants and from specific industrial operations. We are, therefore, searching the commercial market for equipment and devices that are most suitable for the particular needs of the Air Force. The main items of interest are listed on the attached sheet, but this is not intended to exclude any additional factors that may be pertinent.

Automated on-line instrumentation will be preferred, but for parameters that cannot be determined in this manner, other automated or semi-automated procedures will be utilized. If you market equipment that you would like to have considered, please send information including specifications, cost, availability of replacement parts, anticipated maintenance schedules, and any other factors that would assist in evaluation of your product. Duplicate copies of printed material would be helpful.

The time allotted to the collection of information is limited, and a reply at your early convenience would be appreciated.

Yours truly,

T. F. Craft
Senior Research Scientist

TFC:lsg
Enclosure

Figure 1. Form letter sent to instrument suppliers.

Items of particular importance in wastewater at United States Air Force installations:

Hydraulic Loading	Turbidity
Color	pH
Temperature	Dissolved Oxygen
Filterable Solids	Dissolved Solids
Organic Loading (TOC, COD, etc.)	Residual Chlorine
Total Cyanide	Total Oils & Grease
Mercury	Free Oils & Grease
Silver	Cadmium
Copper	Lead
Nickel	Zinc
Iron	Total Chrome
Phenol	Hexa-valent Chrome
Surfactants	Total Phosphates
Nitrates	Organic Phosphates
Nitrites	Total Nitrogen
Conductivity	Flow Meters
Sampling Devices	

Instruments capable of sensing more than one parameter

Figure 2. List of parameters sent to instrument suppliers.

If there was doubt about the utility of a particular device, the supplier was asked for additional information on which to make a decision. No further contact was made with companies whose equipment was deemed inapplicable, inappropriate, or unsuitable. Nor was any additional action required when a reply stated the company had nothing to offer.

If no reply to the first letter was received in a reasonable length of time, a second copy of the form letter was prepared and across the bottom was written in large letters with a red fiber-tipped pen the words "Second Request - Do you have anything to offer?" This second letter brought forth many answers, leaving only about 50 unanswered. It is believed that those companies which did not reply to either inquiry have nothing to offer or do not care to cooperate. No additional attempts at contact were made.

A questionnaire accompanied by an explanatory letter was sent to most of the instrument users whose names were furnished. In a few instances more names were available than needed, and in other cases only ambiguous identifications such as U. S. Geological Survey, Washington, D. C., were given. Preference was given to users where the name of a specific individual was included, although many letters were addressed to the attention of "Waste Treatment Engineer," "Superintendent," or other job-descriptive title. The questionnaire itself was also personalized by typing in the company name and address to whom it was sent. The name, model number, and manufacturer of the instrument was also typed. Copies of the questionnaire and covering letter are shown in Figures 3 and 4. A self-addressed, stamped envelope was enclosed with each questionnaire. Slightly more than 56% of the questionnaires mailed were returned.

The questionnaire was designed to obtain information on which to base a decision on whether a particular device is suitable for Air Force use. It is felt that the value of an opinion of any individual is dependent on his background, training, and experience. As details

(SAMPLE)

Georgia Tech Survey of Wastewater Monitoring Instrumentation

Name: Happy Valley Sewage Treatment Plant, Happy Valley, Georgia 31405

Individual answering questions: Title or position:

Type of wastewater treated: Domestic___ Industrial___ Combined___

How many years of experience have you had in the wastewater field?

Instrument: Model 40 Turbidimeter Manufacturer: XYZ Instrument Co.

How many of these instruments do you have in your plant?

How long have they been in operation? Estimated total useful life: ___yrs.

Do you consider the instrument satisfactory? Yes___ No___ Partially___

Is it sufficiently accurate for your requirements? Is it reliable?

How frequently is calibration necessary?

Is it simple to operate? Is scale or meter easily read?

Are knobs or controls (if any) readily accessible? Too accessible?

What are the undesirable features of the instrument?

Is there anything in your normal operation that causes any interference with the instrument?

How often do you routinely service it? Is it difficult to service?

How often does it break down?

Can you (or someone in your plant) repair it? Is repair difficult?

How much time does it take? Are spare parts readily available?

Is outside help necessary for repair?

About how long does it take to get outside help?

Do you have instruments of any other brand for the same purpose as this one?

Manufacturer: Which do you prefer?

Why?

If you were building a new plant, which brand would you buy?

Any comments would be welcome - write on the back of this page or a separate sheet.

Your cooperation is greatly appreciated!

Figure 3. Questionnaire sent to instrument users.

ENGINEERING EXPERIMENT STATION

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA 30332

March 1, 1973

(SAMPLE)

Mr. D. A. Ellison, Supt.
Happy Valley Sewage Treatment Plant
Happy Valley, Georgia 31405

Dear Mr. Ellison:

As consultants to the United States Air Force, we are seeking information on instruments for wastewater sampling and monitoring that are suitable for Air Force requirements. It is believed that the most reliable information will come from those who have had personal experience with the instrument for a significant length of time.

The manufacturer of the instrument noted on the enclosed sheet has given us your name, and it would be greatly appreciated if you will share with us your experience with this equipment. A self-addressed stamped envelope is enclosed for easy return of the completed questionnaire. Your response will be held in confidence, and will not be individually revealed. We solicit your cooperation and look forward to hearing from you in the near future.

Yours truly,

T. F. Craft, Ph.D.
Senior Research Scientist

Figure 4. Form letter sent to instrument users.

of this sort did not appear worthwhile to request, only the single question along this line was included: How many years of experience have you had in the wastewater field?

GENERAL DISCUSSION OF RESULTS

The majority of the returned questionnaires reported satisfaction with the instrument in question, although an appreciable number indicated only partial satisfaction, and some revealed dissatisfaction. Approximately 25% of those replying made comments ranging from a brief handwritten sentence to multi-page typed letters. These added comments were regarded as highly significant as they furnished details that could not have been elicited by any questionnaire of reasonable length.

It was obvious that many respondents felt that a simple "yes" or "no" was insufficient and further explanation was needed. The nature, cause, and correction (or lack of correction) of various difficulties was frequently explained, and justification for adverse comments was often included. This type of response was far superior to the reply which indicated only partial satisfaction, but answered all other questions in an affirmative manner. In contradistinction, however, was the much more prevalent type which included one or more negative answers but still considered the instrument satisfactory. It is believed that this reflects a pragmatic attitude on the part of the respondents. Individuals experienced in wastewater treatment and particularly in wastewater monitoring are well aware of inherent difficulties, and therefore recognize and accept the limitations of equipment available at present. Based on the replies to questionnaires, discussions with numerous operators and engineers, and personal experience, the concensus is that most instruments require frequent personal attention if they are to function in any acceptable manner. It appears to be a general opinion that all monitoring instruments could be improved and many additional instruments are needed.

SECTION III

TESTS OF INSTRUMENTS

Some of the information received concerned recently developed instruments for which no appreciable user experience existed. Three of these devices which seemed particularly useful were borrowed from their manufacturers and evaluated under field conditions.

Tests were carried out at the Flint River Water Pollution Control Plant of the City of Atlanta. This plant was chosen because its influent was considered to be more like a typical Air Force waste than the influent to any of the other local treatment facilities. About one-third of the plant influent consists of industrial wastes which are produced at the Atlanta airport, a large automobile assembly plant, and other manufacturing facilities. The balance of the plant flow comes from areas that are primarily residential.

The plant was placed in operation a year ago. At present, about 3 million gallons per day (MGD) of influent is being treated, although the design capacity is 6 MGD. It was intended that this facility serve as a pilot plant for the City of Atlanta, and a high degree of flexibility has been provided. In addition to the usual features of an activated sludge plant, there are both aerobic and anaerobic digestors. Additional tanks are provided for thickening of digested sludge through use of polymers, but can be used for other purposes. A well-equipped and staffed laboratory is a vital part of this plant and furnishes analytical services for several Atlanta treatment plants.

The physical arrangement of the plant includes spacious tunnels around the outside of all the major basins. These subterranean passageways house most of the pipes, valves, pumps, and electrical equipment. Two of the instruments tested were installed in this tunnel where it was convenient to utilize gravity flow of sewage and effluent into the instruments.

TOTAL OXYGEN DEMAND ANALYZER

This instrument manufactured by Ionics, Inc. was installed at a location in the tunnel where a continuous flow of liquid could be obtained from the channel leading from primary settling basins to the aeration basins. It was reasoned that this would be the optimum point in the treatment sequence to determine oxygen demand, as the air supply to the aerators could then be regulated accordingly. A photograph of the installed test instrument is shown in Figure 5.

The principles of operation of this instrument are described by the manufacturer as follows:

"The Total Oxygen Demand measurement is achieved by continuous analysis of the concentration of oxygen in a combustion process gas effluent. The oxidizable components in a liquid sample introduced into the nitrogen carrier gas stream flowing through the combustion tube are converted to their stable oxides by reaction at the surface of a platinum catalyst at 900°C. This disturbs the oxygen equilibrium at the platinum surface which is restored by a controlled oxygen concentration in the carrier gas stream. The momentary depletion in the oxygen concentration in the carrier gas is detected by a platinum-lead fuel cell and is recorded as a negative oxygen peak on a potentiometric recorder.

"The Total Oxygen Demand for the sample is obtained by comparing the recorded peak heights to a calibration curve of peak heights versus TOD for standard potassium acid phthalate solutions. The TOD for the standard solution is based on experimentally observed reactions in which carbon is converted to carbon dioxide and hydrogen to water. Observed reactions also indicate that during TOD analysis, combined nitrogen is converted to nitric oxide and sulfide ions to a constant oxidation state approximating sulfur dioxide."[1]

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[1] Total Oxygen Demand Analyzer Operating Manual, Revised Edition, Ionics, Inc., Watertown, Mass. (April, 1970)

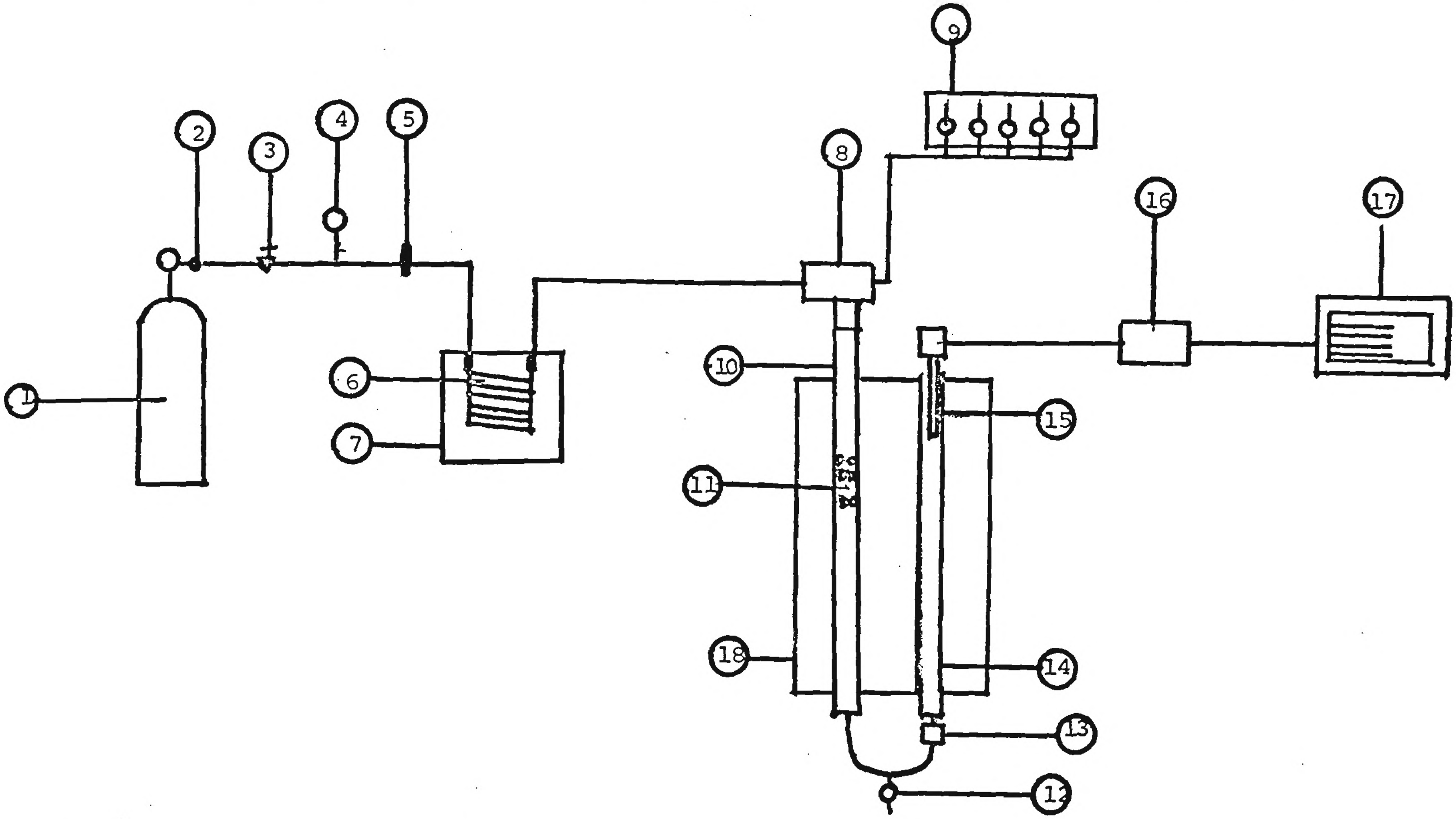
Figure 5. Total Oxygen Demand Analyzer of Ionics, Inc. installed at Flint River Plant, Atlanta, Georgia.

These principles apply to both the Process Model tested and the Model 225 which has been available for several years. The Model 225 is designed for manual injection of samples; the Process Model provides a continuously operating valve which collects 20 μl samples and injects them into the furnace every 3 minutes. A continuous flow of the liquid to be analyzed to the automatic valve is necessary. A diagram representing the various components of the instrument is given in Figure 6.

Considerable difficulty was encountered in maintaining flow through the small diameter temporary sampling line that was used. The liquid contained appreciable amounts of flocculent suspended solids which gradually accumulated on all surfaces in contact with the liquid. It was unusual for the flow system to remain unclogged for more than 6 or 8 hours, although on one occasion it functioned unattended for about 30 hours. Several arrangements for filtering the flow were tried, but provided little, if any, improvement.

It appears that a filtration or solids separation system of some type would be mandatory for a permanent installation involving a liquid carrying more than about 10-15 parts per million of suspended solids, although this would depend on the nature of the solids and the size of individual particles. However, the solids exert an appreciable demand for oxygen, and results will be biased if they are removed. In the practical situation of a treatment plant this is unlikely to be of any significance, as very precise control of the air supply is not normally possible.

The test instrument was installed by a factory representative who checked and adjusted the various parts of the instrument. After a few days of preliminary familiarization with the equipment several 4-day runs were made. During the first test periods the gas flow was turned on and the instrument energized on Monday afternoon, and the sampling valve and recorder on Tuesday morning. This interval allowed the furnace to reach operating temperature (2 hours is actually sufficient) and the enclosure housing the fuel cell and permeation tube through which oxygen enters the system to reach thermal equilibrium. This enclosure is heated by a thermostatically controlled 25



1. Cylinder of prepurified N_2
2. Cylinder pressure reducing valve
3. Instrument N_2 pressure regulator
4. N_2 pressure indicator
5. Critical orifice
6. Silicon rubber permeation tubing
7. Low temperature furnace - 55° C
8. Rotary sampling valve (RSV)
9. Sampling system
10. Catalyst furnace tube
11. Platinum catalyst bed
12. Drain valve
13. Expansion volume
14. Detector furnace tube
15. Detector
16. Drift corrector circuit
17. Recorder
18. High temp furnace

Figure 6. Outline of Process Model TOD Analyzer

watt light bulb, and several hours are needed to reach the design temperature of about 40°C. It was noted that the on-off operation shortens the life of the furnace tube, and it was thereafter left on continuously.

The instrument was calibrated with potassium acid phthalate solutions of three known concentrations, and the response was quite linear. The instrument was then allowed to operate continuously on the effluent from the primary settling basins. It was noted that the measured TOD varied during each 24-hour period. The height of the peaks on the recorder chart increased and decreased slowly in regular fashion, producing smooth gradual curves. An occasional peak protruded considerably above adjacent peaks, but this is believed to be due to inclusion of a bit of solid matter in the injected sample, and no particular importance is attached to these infrequent occurrences.

The significance of the TOD vlues was evaluated by comparing them with the total organic carbon (TOC) content of the liquid. Samples for this purpose were collected at intervals, and the TOD was noted at the time of each collection. TOD values were quite proportional to TOC values obtained with a Beckman Model 915 TOC Analyzer. The experimental values were plotted as shown in Figure 7.

The instrument tested had been used as a demonstrator, and was received with a faulty voltage regulator that caused the furnace relay to chatter four or five times each time it was energized. This had no apparent effect on the operation of the furnace, but the noise was annoying. Examination of the electronics revealed some noise when the system was idling, and a slow drift was also present. Under normal conditions the rate of drift was slow enough to be overcome by the automatic zeroing feature.

As time progressed, the peak heights on the recorder chart became erratic, and the needle was frequently off scale on the high end. Matters grew rapidly worse and considerable time and effort were required to restore the instrument to normal. The difficulty was due in part to lack of experience by the operator but also to the complexity of the system and the numerous possible sources of trouble. During this period

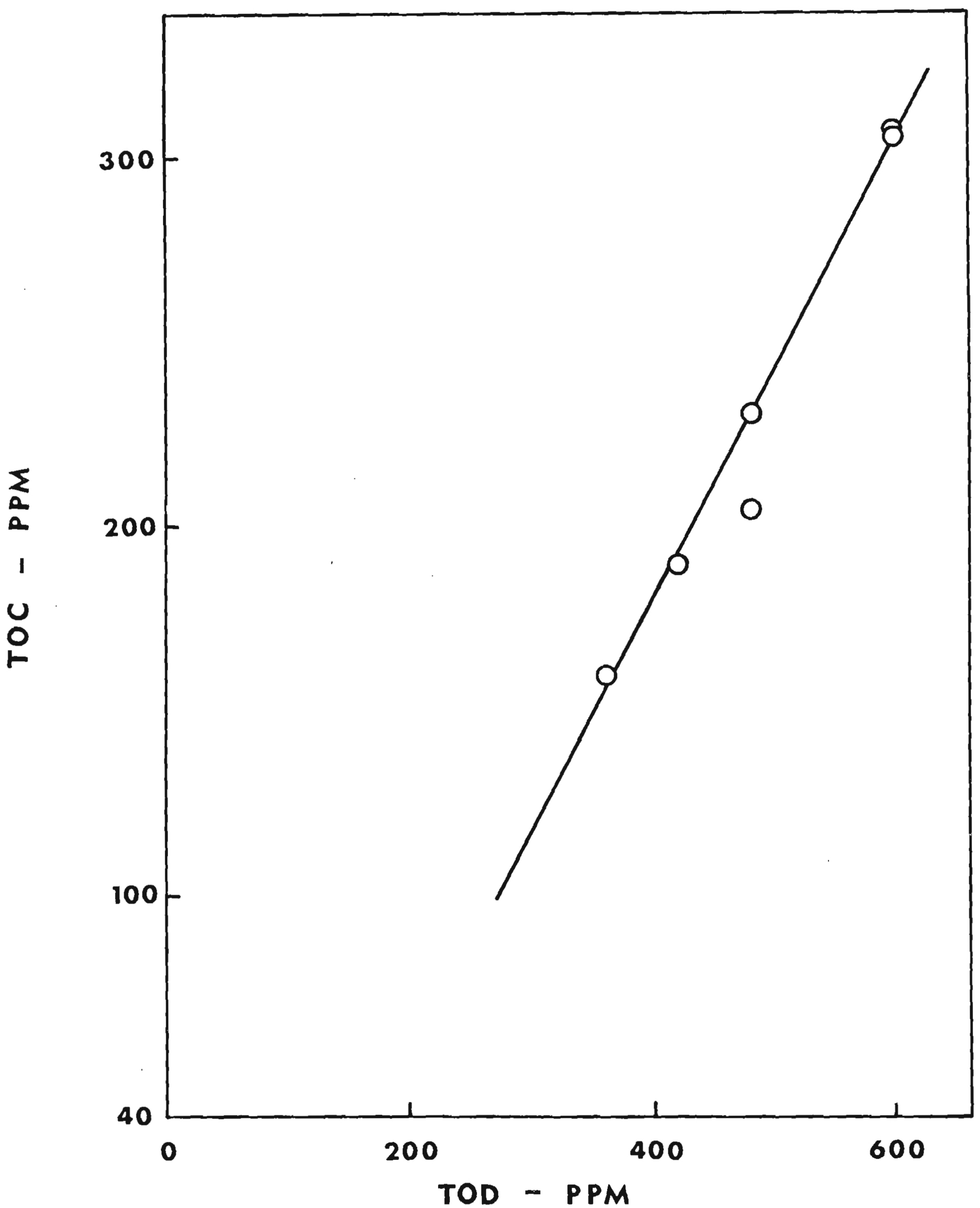


Figure 7. Correlation of TOD and TOC for primary sedimentation effluent, Flint River Plant

of malfunction the light bulb in the cell chamber burned out. When replaced, it burned continuously due to the failure of the relay in the thermoregulating circuit.

Several things contributed to the trouble. The flow meter in the carrier gas line is mounted inside the instrument cabinet and can be seen only at an angle by raising the lid. It was discovered that the flow had decreased to an undesirably low value of 0.10 cfm and was therefore raised to 0.20 cfm. The presence of air leaks in the system was indicated by a fuel cell output of about 75 microamps when the oxygen permeation tube was replaced with a non-permeable connector. Under these conditions the output should have been less than 50 microamps. It was also found that the platinum catalyst in the furnace tube was badly fouled and had dropped from the center of the furnace into a much cooler location at the bottom of the tube. The tube itself was somewhat crystallized and had become partially opaque; it was replaced.

Subsequent operation was continued for a week without additional serious problems. The instrument was then relocated to another position in order to sample plant effluent. Sample delivery was much less troublesome because of the low suspended solids load, and the instrument performed satisfactorily for several days at which time the test was terminated.

The conclusions drawn from this plant experience are in general agreement with the findings of a previous evaluation of the Model 225 TOD Analyzer [(2)] in which it was noted that the instrument is a rapid means for determining oxygen demand in domestic sewage treatment plant samples with the exception of influent sewage. It was also suggested that COD/TOD and BOD/TOD ratios could be established experimentally and would allow promptly-obtained TOD values to be used for plant control.

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2 Technical Report, Evaluation of Ionics' Model 225 Total Oxygen Demand Analyzer, EHL(K) 69-27, USAF Environmental Health Laboratory, October 1969, unclassified.

It appears that the Process Model could be used satisfactorily for control or monitoring only when it is under the direct supervision of a trained individual who will provide regular, careful maintenance. The complexity of the instrument necessitates a knowledgeable approach to trouble-shooting, and an electronics specialist is required if difficulties arise in the electronics section. This equipment is unlikely to function acceptably in unattended operation for extended periods of time, and should be considered only where constant, high-quality attention can be maintained.

SPECIFIC ION ELECTRODE MONITOR

The major advantages of specific ion electrodes as analytical devices are their ability to cover a very large range of concentration, their almost immediate response to changes in solution composition, and the need for little or no sample pretreatment, since neither turbidity nor color is a factor. Drawbacks include a limit of precision on direct measurement of about $\pm$ 2 percent for a monovalent ion, and $\pm$ 4 percent for a divalent ion. Also, most electrodes do have some interferences from other ions and, while these can usually be overcome, prior knowledge of the qualitative composition of the sample is required.

Although chamical sensing electrodes have long been used in laboratories, it is only recently that they have been used in the field for any purpose other than pH measurement. Their use has met with somewhat limited success, possibly through misapplication and uncompensated interferences, but also because of hostile environmental influences.

The 1000 Series of instruments has been developed by Orion Research to provide for each ion monitored a suitable chemistry to eliminate interferences, cause or present formation of complexes as required, and prepare the sample for accurate measurement by an electrode. Additionally, the system components are housed in a substantial NEMA 12 case where the critical sensing assembly is electronically thermostatted to produce "laboratory conditions."

Orion Research provided a Series 1000 Fluoride Monitor for evaluation. Although this series of instruments will eventually include versions for many different ions, they are not all available as yet. A fluoride sensing unit was immediately available and was accepted for testing even though fluoride content of wastewater is seldom of interest. The Atlanta water supply is fluoridated, and the monitor could therefore be tested on an ion known to be present and whose concentration would probably vary.

The instrument arrived in a very substantial but light weight shipping box. Shock absorbing material inside provided complete protection in transit. The instrument was installed as shown in Figure 8 at the Flint River Plant in a location convenient to a sampling line for plant effluent. Set-up services were provided by an Orion engineer who made the necessary mechanical and electrical connections and added a membrane flow-past filter to the sample line. He made a few minor adjustments, calibrated the instrument, and demonstrated its operation. Fluoride determination requires only a single reagent, TISAB (total ionic strength adjustment buffer). TISAB buffers the solution at pH 5.0-5.5 to avoid hydroxide interference or the formation of hydrogen complexes of fluoride. It contains CDTA (1,2 cyclohexylene diaminetetraacetic acid) to preferentially complex any aluminum in the sample. TISAB also provides a constant high ionic strength background to "swamp out" differences in sample ionic strength.

The monitor was allowed to run continuously, with daily inspection. The only difficulty was with the sample feed line which occasionally became clogged at the orifice of an inserted flow constrictor. Values of fluoride remained rather constant at about 0.8 ppm during dry weather. When the volume of the plant flow was increased by storm water the concentration dropped to about 0.6 ppm. Values were compared frequently against those given by an Orion laboratory model fluoride detector which was calibrated before each use against solutions of known fluoride content.

The various components of the instrument all performed well during the test. The automatic calibration feature which restandardizes the instrument once each 24 hours performed according to specifications. Only small adjustments occurred during these calibration sequences, as there was little base line drift and the response was quite stable.

Figure 8. Series 1000 Fluoride Monitor of Orion Research installed at Flint River Plant, Atlanta, Georgia.

Based on this experience with the fluoride monitor, it is concluded that the concept of the device is excellent. The manufacturer specializes in specific ion electrodes, and an optimum chemical system will be provided for each ion to be monitored. It appears that this series of instruments will be satisfactory for wastewater monitoring in many applications.

DISSOLVED OXYGEN ANALYZER

Delta Scientific loaned a Series 8010 Automatic Dissolved Oxygen Analyzer/Controller for evaluation. This instrument uses a patented polarographic membrane probe for which claims of superiority are made. The probe consists of gold and silver electrodes with a connecting reservoir containing buffered potassium chloride electrolyte, and a prefabricated easily replaceable permeable Teflon membrane. Because oxygen is consumed in the reaction which generates the electric current in the probe, it is essential that a fresh supply of sample is available at the probe tip. A sample agitator consisting of a small paddle is attached to the probe housing. Back and forth motion of the paddle near the membrane assures a fresh sample and avoids entrapment of solid matter present in the water. A thermistor automatically corrects for changes in water temperature. The probe is designed for a minimum service period of nine months between electrolyte changes. The consumable materials in the probe are sufficient for a minimum of 3 years of probe life at ambient operating conditions.

For use as an automatic controller, two knobs permit setting of low and high control points directly on the meter scale. In operation, should the oxygen level reach either control point, a signal light is turned on, and a 5-ampere relay will be activated to perform the appropriate control function. The relays may be set to latch and hold or unlatch, as desired. The terminals can also be wired to reset the relays automatically. The instrument covers the full range of dissolved oxygen in three steps: 0-2, 0-10, and 0-20 parts per million.

The analyzer is housed in a fiberglass case with a hinged gasketed cover. Four screws hold the cover closed, and some time is required to remove and replace them. The instrument is shown in Figure 9.

Figure 9. Dissolved Oxygen Analyzer/Controller of Delta Scientific installed at Flint River Plant, Atlanta, Georgia.

The evaluation was carried out at the Flint River Plant. The probe was attached to the end of a pipe and placed in the discharge end of the activated sludge aeration tank. The analyzer/controller unit was attached to a nearby post near an electrical outlet. This post is under a small shed roof, but receives little protection from the weather.

The probe was standardized against a Yellow Springs Instrument Company Model 54 Dissolved Oxygen Meter. The instrument was kept in continuous operation for 6 weeks. The oxygen readings were compared frequently with those of the Yellow Springs instrument which was frequently recalibrated in the laboratory. The readings of the two usually agreed within 0.1-0.2 ppm when the total dissolved oxygen was in the 1.0-2.0 ppm range.

Occasionally the probe was removed from the tank for inspection. Some solid matter accumulated on the probe, but the critical membrane area was kept clean by the vibrating paddle. No evaluation of the control function was made other than to note the operation of the relays when the limit knobs were turned.

It is concluded from the performance of this device during the test period that it is very useful and will probably prove satisfactory under normal conditions.

SECTION IV

RECOMMENDATIONS FOR ANALYTICAL INSTRUMENTS

To facilitate the use of this report, a very brief description of laboratory techniques is included for each parameter. In most cases the methods are those given in Standard Methods [3] although a few others have been added.

It is felt that the most useful instruments for wastewater monitoring are those which give direct, immediate response to variations in the measured parameter. Temperature, turbidity, and dissolved oxygen, for example, can be readily determined in this fashion.

Next in utility are devices that require the addition of one or more reagents to the sample stream, followed by detection with a continuously-responding sensor. For instance, total chlorine residual can be detected amperometrically following reagent addition. These types of analyzers necessarily incorporate a time lag between sample induction and read-out of results. The actual time delay depends on the chemistry involved but may range from one to several minutes.

Least satisfactory is equipment that produces answers in a discontinuous manner. Typically a sample is taken in, subjected to chemical or physical treatment, and a read-out is produced. The cycle is then repeated. TOC and TOD are now amenable only to this type of analysis. At the present state-of-the-art, however, for many parameters this type equipment is the only alternative to manually performed laboratory analyses.

It is claimed by the manufacturers of automatic type chemical analyzers that many parameters of wastewater can be measured by their equipment. However, they were not able to furnish information on any specific location where wastewater analysis is being carried out. Inquiries elsewhere

[3] Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Assn., New York, N. Y., 1971

failed to discover any users. However, several users of instruments that operate by combustion of a sample and subsequent detection were located. It seems that in some instances discontinuous-response machines may prove satisfactory, but other types are preferred, when available.

Prices included in the following discussions are intended for comparative purposes only. These list prices were current in March, 1973, but are, of course, subject to change. The salvage value of worn-out or obsolete scientific instruments is low. Components of some instruments may find secondary usage for other purposes in some instances. Otherwise, their remaining value would be as scrap.

AMMONIA

Ammonia analysis in the laboratory is performed colorimetrically, but a preliminary distillation step may be required. Specific ion electrodes for ammonia are available and may be used for continuous monitoring. (See Specific Ion Electrode Monitor, Section III.) Delta Scientific has recently offered a continuous spectrophotometric analyzer for ammonia, but user information is not available. AutoAnalyzer equipment is reported usable for this determination. See Nitrogen topic in this section.

CADMIUM

The methods available for the determination of cadmium are colorimetry, atomic absorption, polarography, and chemical sensing electrode. An Orion Series 1000 Monitor equipped with a cadmium electrode seems promising for on-line applications. See Section III for information on this instrument.

CHLORINE RESIDUAL

Many satisfactory laboratory procedures are available for the determination of chlorine residual in relatively clean water. However, the analysis is much more difficult in the presence of appreciable organic matter as chlorine combines readily with organic compounds, particularly those containing amine nitrogen. Residual chlorine may therefore exist in either free or combined (chloramine) form. Sewage chlorination is seldom carried to the point necessary to produce free available chlorine and the differentiation between free and combined states is not ordinarily made. Using measures designed to avoid numerous possible interferences, analysis can be made by iodometric procedures, amperometric titration, or various colorimetric techniques.

Chlorine residual is a parameter of great importance in water treatment, and continuous on-line analyzers are widely used in the water utility industry. These instruments operate amperometrically. The sample passes a pair of electrodes of dissimilar metals. The polarization of the more positive metal electrode prevents the passage of current in the absence of an oxidizing agent. Traces of oxidizing agents cause depolarization, and a current proportional to the concentration of oxidants is generated if a constant potential is maintained across the electrodes. Instruments of this type are available from at least three manufacturers.

Wallace and Tiernan customers report favorably on the W&T Chlorine Residual Analyzer for wastewater. The analyzer cell is identified as Series A-792. In a modular cabinet with recorder and chlorinator controls, the complete instrument is priced in the range of $3500-3800. Other configurations without recorders are in the $2300-2600 range. This system is recommended because of its substantial construction and long history of successful use.

Capital Controls Model 872 Chlorine Residual Analyzer and Monitor has been satisfactory for most users that responded to the questionnaire. The manufacturer claims maintenance-free operation. It is priced at $1700 which includes a recorder.

Fischer and Porter offer residual chlorine analyzers under the trade name "Anachlor." No user information was available, but the analyzer with recorder is approximately $2900.

A continuous residual chlorine analyzer operating on colorimetric principles is offered by Hach Chemical Co. This instrument is relatively new to the market, and no user information is available. It is priced at $3000 plus freight. A recorder is available at $650. A similar instrument is marketed by Delta Scientific at approximately the same price.

CHROMIUM

Several methods of analysis are available for the determination of total chromium and hexavalent chromium. The latter is of considerable importance because of its high carcinogenic potential. Procedures applicable to wastewaters include atomic absorption (for total chromium only) and colorimetry for both hexavalent and total chromium.

A continuous colorimetric analyzer for hexavalent chromium has been offered by Hach Chemical Company, but user response to inquiries about it were generally negative. Hach advises that this device is being redesigned at present, and a greatly improved version will be made available in the future.

Delta Scientific also offers a colorimetric analyzer for hexavalent chromium. Only a few of these are in use at present, but the manufacturer reports no difficulty with the instrument. It is claimed that the components which come in contact with the sample and reagent are constructed of exceptionally durable materials. Another version is available for detection of total chromium. These instruments are in the $3000 class.

AutoAnalyzer analysis for hexavalent chromium is also available, according to Technicon Instrument Corporation.

COLOR

The term "color" is used to mean the color of water from which turbidity has been removed. "Apparent color" includes color due to dissolved substances and also that due to suspended matter. Color of relatively clean waters is ascertained by visual comparison of a sample with known concentrations of colored solutions or calibrated glass color disks.

Color is not normally a parameter of intent in sewage, but is often important in industrial wastes. The color of a waste is considered to be the color of the light transmitted by the solution after removal of suspended matter. In practice, a sample of waste is filtered and the color is measured with a spectrophotometer. The results are expressed in terms which describe the sensation realized when viewing the waste. The hue (red, yellow, green, etc.) is designated by the term "dominant wavelength," the degree of brightness by "luminance," and the saturation (pastel, pale, etc.) by "purity."

Continuous automatic spectrophometric analyzers for color are available from Hach Chemical Company ($2600) and Delta Scientific ($3000). They operate by comparison of the sample with APHA platinum cobalt color standards and are intended primarily for potable water supply monitoring and for certain industrial uses. Due to the wide variety of hues possible in wastewater, their use for this purpose is not recommended.

CONDUCTIVITY

Conductivity is a generalized parameter which provides information concerning the total ionic concentration of the sample measured. Where only two ions are present in a sample, the conductivity gives an accurate measure of their concentration. Wastewater samples seldom have such a simple system, so that accurate correlations can not be read between the electrical value in micro mhos and the salt concentration. Empirical correlations between micro mhos and other parameters can frequently be developed.

Conductivity can be measured by a resistance method using submerged electrodes or by an inductance method where the sample is placed in a coil transmitting a low frequency AC. In either case the sample may be stationary or moving. The submerged electrodes must use a high frequency alternator to prevent polarization but they do give high accuracy at low conductivity, low salt concentrations. The inductance method does not require contact with the sample, and so less frequent maintenance may be possible but there is less sensitivity at low conductivities.

The resistance method is by far the more commonly used technique. Immersion or flow-through cells equipped with platinum electrodes are normally used in laboratory applications. Electrodes constructed of stainless steel or other common durable metal are widely used for continuous monitoring and field studies. Greatest accuracy is obtained when the actual resistance measured is in the range of 500 to 10,000 ohms, and this requires different cell and electrode configurations with matching electronic components for high and low ranges of conductivity.

The inductance method is recommended for measurement of solutions of high conductivity that are corrosive or which contain materials that will coat or otherwise interfere with electrodes.

None of the instrument suppliers contacted offered information on users of instruments to measure only conductivity, although this parameter is commonly included in multisensing devices. A number of both well-established and newer companies offer conductivity instruments. Due to the relative simplicity of these devices they are presumed to be generally satisfactory, although no user data was available.

COPPER

Several methods of copper analysis are possible, including atomic absorption, spectrophotometry, colorimetry, emission spectroscopy, polarography, neutron activation analysis, and specific ion electrode. Continuous monitoring equipment of several types is presently on the market, but no user information was available on any of them.

A polarographic device, Type 17H1000 Copper Analyzer, is manufactured by Fischer and Porter. The instrument is very similar in physical configuration to their chlorine residual analyzer. Price is about $6000.

Hach Chemical Company markets a Series CR-2 monitor for copper. It is a colorimetric instrument and is priced at $2600.

Delta Scientific also offers a photometric instrument at approximately $3000.

The Orion Research Series 1000 monitor for copper is considered potentially useful. See discussion in Section III.

Technicon Instruments Corporation advertises the use of their Auto-Analyzer for copper.

CYANIDE

The results of a cyanide analysis may vary according to the form in which the CN group exists, as the cyanides show varying degrees of chemical activity. Simple cyanides may be converted readily to HCN for analysis, but complex cyanides, such as those of iron, show greater resistance to decomposition to HCN. Complexes of cobalticyanides decompose very slowly. Laboratory procedures usually include one step to form free cyanide ion, and others to avoid interferences. Determination of cyanide ion can then be performed by silver nitrate titration or by a colorimetric procedure. A specific ion electrode for cyanide can be used for continuous observation. The Orion Series 1000 Monitor is available for total cyanide. See Section III for comments on this series of instruments.

Technicon Instruments Corporation reports that cyanide analysis can be performed automatically with their AutoAnalyzer equipment, but detailed information is not available.

DISSOLVED OXYGEN

There are two major types of commercially available dissolved oxygen (DO), on-line instruments. One commercial instrument uses the potential developed between a thallium electrode and a reference electrode (calomel cell). Most other DO instruments are polarographic with imposed electrical current: some laboratory instruments using the polarographic principal have a galvanic electrode pair, but these sensors are not used for extended periods of on-line monitoring. Because enzymes in domestic wastewater depolarize the polarographic cathode, all polarographic systems are separated from the samples by a membrane. The oxygen molecule must diffuse into the electrolyte surrounding the electrodes.

The thallium electrode system, Union Carbide-Ionics, depends on the solution pressure (corrosion) of the thallium electrode by DO. The amplifier is similar to those used with pH and ORP units. The electrodes do require cleaning, adjustment and eventual replacement of the thallium. The thallium electrode is relatively massive and very rugged however.

The polarographic electrode system should be large enough to have a large reservoir of fluid to reduce maintenance frequency. The sample surface of the membrane must be kept clean and clear. It should have a rather rapid movement of the water over its surface. Honeywell does this with screens and a submerged pump which discharges directly onto the membrane or with a jet of sample against the membrane in its river monitor. Delta Scientific uses a vibrator paddle, close to the membrane. Weston-Stack (Leeds & Northrup) has a small propeller mounted directly below the membrane. Observations of installations, where the sample is not in rapid motion against or past the membrane, indicate the futility of the operation. Cleaning of jets or mechanical devices requires maintenance but the motion of the sample is essential.

The replacement of the membrane on a number of the early polarographic models was tricky and critically important. Newer units have improved designs. The measurement of DO has become so important in the environmental field that the competition has encouraged development of several excellent instruments.

One laboratory has used several Honeywell DO sensors and has had excellent experience with them. A small single cell battery is required to produce the current flow through the sensor and it must be replaced periodically. Questionnaires about the DO sensor by Weston-Stack which is used by Leeds and Northrup have been favorable and based on the excellent professional reputation of the firm their equipment for DO is recommended. The Delta Scientific DO sensor has been tested by us and found to be highly satisfactory (a description of our test is given in Section #3).

On the basis of direct discussions and observations of those operating the thallium potentiometric DO units, the system is not recommended for use in wastewater monitoring.

DISSOLVED SOLIDS

"Dissolved solids" is the term used in the past that corresponds to the term "filtrable solids." The latter designation is more precise, however, because the distinction between suspended and dissolved matter is not very clear, and depends on many variables in the separation procedure. See comments under "Filtrable Solids."

FILTRABLE SOLIDS

"Filtrable residue" is the term applied to the material that remains after evaporation of a sample of filtered water and its subsequent drying in an oven at a definite temperature. The quantity of residue obtained depends on many variables including the chemical and physical nature of the material in suspension, the pore size of the filter, and the area and thickness of the filter mat. Residue determinations are therefore not subject to the usual criteria of accuracy.

Under suitable conditions specific conductance might be used to estimate filtrable residue. Only electrolytes are detected by conductivity measurements, but this is acceptable if the ratio of electroyltes to total dissolved solids is reasonably constant. For a given waste stream it may be possible to evaluate the correlation between specific conductance and filtrable residue by comparing values for many samples taken over a significant period of time.

Density measurements are also possible for the determination of filtrable residue, but are customarily used only for brines or other liquids with high solids content.

No continuous, automatic, or semi-automatic devices for determination of filtrable residue were located.

HYDRAULIC LOADING

Measurement of flow is essential in wastewater monitoring, and can be done in a number of ways. Devices used include gravimetric and volumetric containers, orifices, weirs, pipe bends, nozzles, parabolic flumes, velocity meters, Palmer-Bowlus flumes and Parshall flumes. For satisfactory application, it is necessary that the selected device not offer any obstruction to the passage of suspended or floating solids. Thus sharp-edged and small orifices, nozzles that are not smooth, notched weirs, and moving-part meters are not recommended, although they may be acceptable where self-cleansing velocities are maintained.

The most satisfactory measuring devices appear to be Parshall flumes equipped with level-sensing instruments. The advantages of a Parshall flume as a measuring device include an insignificant loss of head, measurements can be made in open-channel flow, the flume is self-cleansing, and there are no moving parts. Many level-sensing devices are available, and this method of flow measurement is widely used and is recommended.

If pipe flow is involved, a magnetic flow meter is recommended. The operation of this type flowmeter is based on Faraday's law which states "the voltage induced across any conductor as it moves at right angles through a magnetic field is proportional to the velocity of that conductor." Here the liquid flowing through is the conductor, and it is necessary only to determine the voltage generated. Users of meters of this type express general satisfaction. Care must be exercised in the installation of magnetic flowmeters to avoid interferences from other electrical equipment.

IRON

Atomic absorption spectrophotometry is the preferred method in the laboratory for the analysis of iron. Several colorimetric procedures are available, some to overcome the effect of interfering substances and others to differentiate between ferrous and ferric iron.

Hach Chemical Company offers a continuous monitor for iron in their Series CR2. High and low range versions priced at $3400 and 3200, respectively, are available to detect both soluble and suspended iron. The instrument continuously adds reagents to the sample stream, and iron is detected colorimetrically. The manufacturer suggests its use in iron removal systems, boiler water, and deionizer effluent. User response indicated a need for a very clean sample, which may require elaborate preliminary filtration. Mechanical difficulties are prevalent, the response time is approximately 20 minutes, and output may be non-linear.

Delta Scientific offers a spectrophotometric analyzer for continuous on-line use at about $3000. No user information was available.

Total soluble iron can be detected by AutoAnalyzer equipment, according to Technicon Instruments Corporation, but no technical details or user information was provided.

LEAD

Determination of lead can be made by atomic absorption spectrophotometry, polarography, or colorimetry. A chemical sensing electrode for lead is also available. An Orion Series 1000 Monitor equipped with such an electrode may be suitable for on-line use. See Section III for information on this instrument.

MERCURY

For determination of mercury at the low levels ordinarily encountered in wastewater, only two techniques have proven satisfactory. These are atomic absorption spectrophotometry and neutron activation analysis. The necessity of utilizing a nuclear reactor for neutron activation has limited this method to research studies and standardization of atomic absorption techniques.

A small laboratory instrument for flameless AA determination of mercury is the Coleman MAS-50. It detects only inorganic mercury, however, unless the sample receives preliminary treatment.

An on-line mercury-in-water analyzer has been developed by Olin Custom Analytical Instruments. It is essentially an atomic absorption spectrophotometer with automated sample handling and read-out. It operates in discontinuous fashion, processing discrete samples successively. It is priced in the $25,000 class, and has not found widespread use.

MULTI COMPONENT SENSOR UNITS

When one considers multi component sensor units, the question of choice is obviously colored by unfortunate experiences with a specific parameter. Because different parameters are included in the multi component systems of various manufacturers, it is difficult to compare systems without indicating specific parameters which are also discussed elsewhere.

The manufacturer may design a multi component system to include hydraulic features to give optimum operation of each parameter. Thus the optimum operation of the DO unit in the Honeywell Monitor requires a jet, but the jets clog readily with sand and, therefore, the jet requires maintenance that depends on river quality. To eliminate the need for frequent maintenance during storms a purchaser has eliminated the jet and thus vitiated the accuracy of the DO unit. The same purchaser has another company's multiunit K.D.I. system where the DO unit is in the deadend corner of a poorly designed box. Meaningless DO data are recorded. The other parameters may be doing a fine job.

The needed accuracy or range of the turbidity system will define the identity of the system to a large extent. Where it is necessary to monitor a low range turbidity accurately, a Hach or Honeywell turbidity unit is recommended. Where higher concentration ranges are important, then an Ionics unit can be used, but the Ionics turbidimeter cannot be recommended for low concentrations.

On the basis of experience in our laboratory, a Honeywell pH meter cannot be recommended, but other users have given fine reports of their multi sensing devices and Honeywell's broad experience in Process Control makes them a prime contender for the multi sensing system. The user replies show that Honeywell has the second largest number of satisfied people.

Schneider Instrument Company has provided excellent equipment for the Ohio River Valley Commission and is considered very favorably by ORSANCO.

Leeds and Northrup has assembled a multi component system which uses components from several smaller companies along with their standard items.

Hydrolab Water Quality monitor has the most satisfied users, but several of them find difficulties with specific components. One has used a specific ion electrode as a component but did not find it satisfactory. The sensors were operated at depth in a lake; this may well have contributed to their difficulties.

Automated Environmental Systems has a number of multi component products. These are generally accepted, but again, individual components have given a particular user trouble.

Whitney Montedoro Corporation has users who are generally satisfied with their systems of multi component monitors.

A number of smaller companies such as Delta Scientific can mount their individual component sensors in a multi component housing but there is no single mounting to house the sensors as in an Ionics or Honeywell system.

A choice of a multi component system for a specific recommendation is impossible based on the above comments. The most significant parameters should be carefully considered and may well define the more desirable system.

The early river monitors from Schneider and Honeywell had the following common sensors:

Conductivity
Hydrogen ion, pH
Dissolved oxygen
Temperature
Turbidity

Each individual sensor was wired to its individual amplifier where necessary so that all had a common recorder. Honeywell used a standard 8 point recorder which permitted us to add three weather parameters to aid interpreting the water data because it is much easier to record than interpret data. Storm runoff effects turbidity and possibly the temperature and/or the dissolved oxygen. Thus, river stage should be added to the above list. Air temperature and the sunlight aid in understanding the water temperature and dissolved oxygen (algal activity).

With ion selective electrodes for many parameters, these can be added to the above list as needed without changing any of the design flow patterns or electronic amplifiers. Ion specific electrodes are available for:

floride
chloride
ammonia
sodium
nitrate
calcium
polyvalent ions (hardness)
sulfide

and can be included in the first list by using a multipoint analogue or digital recorder. (This comment is not a recommendation of the reliability or accuracy of the specific ion electrodes.) The amplifiers for the specific ion electrodes are basically the same as the hydrogen ion system and so provide compatible instrumentation including recorder output.

Where different techniques of analysis are employed as in the autoanalyzer equipment another set of parameters can be assembled in a single cabinet with several sensing units. These parameters generally require chemical preparation of a sample for final analysis by a colorimeter or spectrophotometer. Because of the individuality of the chemical solutions required for each parameter, multisensing devices are generally an assembly of "black boxes" for each parameter rather than electrical signals generated by the flow of water over electrodes as in the first group.

Delta Scientific, Hach Chemical Company, and Technicon Instruments Corporation all advertise that their individual parameter analyzers (described in this chapter) may be combined in a single unit. However, no user information was available on the separate components, and it appears that there are few, if any, situations where multiple component systems are in use.

NICKEL

Two colorimetric procedures for the determination of nickel are given in Standard Methods, but both methods are listed only as "tentative." Polarography may be conveniently utilized where equipment is available. Nickel may also be determined by atomic absorption spectrophotometry. No automated or semi-automated equipment is available for the analysis of nickel.

NITRATES

Many procedures are available for the analysis of nitrates. Several colorimetric techniques may be utilized directly, or after reduction of the nitrate to nitrite. Ultraviolet spectrophotometry, polarography, and a specific ion electrode offer other avenues of analysis.

The specific ion electrode appears promising for continuous monitoring. See Section III for information on the Orion Series 1000 Monitor.

Delta Scientific manufactures a continuous spectrophotometric instrument for nitrate at about $3000, but no user data is available.

Technicon Instrument Corporation reports their AutoAnalyzer equipment is available to handle combined nitrate plus nitrite analyses, but user information is not available.

NITRITES

Most laboratory analyses of nitrite involve diazotization and coupling, followed by colorimetric determination of the dye that is produced. A chemical sensing electrode is also available. Nitrite analysis can be handled by AutoAnalyzer equipment, according to Technicon Instrument Corporation, but no user information could be obtained.

The nitrite electrode appears to be the most likely means of obtaining continuous readings. See Section III for information on the Orion Series 1000 Monitor.

Delta Scientific offers a continuous spectrophotometric nitrite analyzer in the $3000 class, but no user data is available.

NITROGEN

Nitrogen may be present in a variety of forms in wastewater, and the quantity of each form may be significant under certain circumstances. In other situations, an evaluation of the total nitrogen content may suffice. Ammonia is a product of microbial activity, and is a commonly encountered form of nitrogen. The albuminoid-nitrogen content of a sample indicates the quantity of proteinaceous matter present. This is associated with animal and plant life normal to aquatic environments.

Nitrite may occur in water as a result of the biological decomposition of proteinaceous matter. Nitrites are not very stable and may be reduced to ammonia or oxidized to nitrates. Nitrates are the most stable form of nitrogenous material found in sewage, and result from the oxidation of organic nitrogen compounds.

Albuminoid nitrogen analysis is performed on samples from which free ammonia has been distilled. Alkaline oxidation converts albuminoid nitrogen to ammonia which is then determined colorimetrically. No continuous or automated procedures are available for this analysis.

Another parameter of significance is "organic nitrogen" which is determined by digestion of the sample after removal of ammonia. If the ammonia is not removed before digestion, the result is known as "Kjeldahl nitrogen" or "total Kjeldahl nitrogen." This procedure of acid digestion followed by titration includes the various forms of nitrogen except nitrites and nitrates. Because of high digestion temperatures required in Kjeldahl analyses, automated procedures do not appear feasible, contrary to the assertions of manufacturers of automatic equipment. No continuous monitors are available for Kjeldahl nitrogen. See Ammonia, Nitrate, and Nitrite topics in this section.

OIL AND GREASE

The ordinary laboratory procedure for the determination of oil and grease is carried out by extraction of a sample with an organic solvent, evaporation of the solvent, and weighing the residue. The initial problem is to obtain a sample that is representative. The oil and grease may be dissolved, emulsified, saponified, or floating on the water surface. It may be necessary to skim the surface to obtain sufficient material for analysis, but this makes it almost impossible to correlate the amount of oil and grease with the total volume of water.

Several sources of error are inherent in extraction processes. Solvents vary in their ability to dissolve not only oil and grease, but other substances as well. No solvent is known that will selectively dissolve only oil and grease. Low-boiling oil fractions are lost unless precautions are taken, and even some high-boiling materials may be lost during solvent evaporation. Certain extractables oxidize readily, and accurate results require added precautions.

One instrument for on-line determination of oil in water was located. It is manufactured by Teledyne Analytical Instruments and is designed for use in refinery effluents and boiler return condensate. The analysis system is based on the measurement of oil by a continuous duty dual beam, process ultraviolet analyzer that compensates for sediment, turbidity, fungus, and other foreign matter. A sample conditioning system allows the measurement of both dissolved and suspended oil, making a total oil measurement, exclusive of other organic compounds not considered oil. A continuous homogenizer disperses all suspended oil droplets and oil adsorbed onto foreign matter, sediment, and fungus to allow a total oil measurement. A sample is fed into both sides of the conditioning system. A high-speed, high-shear homogenizer disperses any oil in the sample, including small and large oil droplets and oil adsorbed onto foreign particles. A portion of the stream is then conditioned to remove all oil, both dissolved and undissolved, and delivers to the analyzer a background sample containing the organic fraction only. The analyzer then subtracts the organic fraction from the oil fraction and reads out total oil only. In refinery use, the analyzer is calibrated with composite oil from the refinery separator.

For the analysis of oil in boiler return condensate, the analyzer is referenced to pure water. The analyzer compensates for boiler additives, carbonates, scale, and rust. Results related only to oil are obtained.

The utility of this system is probably limited by the necessity of calibration against a known standard. The calibration against water recommended in boiler return condensate is acceptable, because absence of other ultraviolet adsorbers is assumed in this situation.

No user information was obtained. The exact designation of the instrument is: Model 661R Oil-in-Water Analysis System, manufactured by Teledyne Analytical Instruments. The basic price is $8500, with an additional $900 for a recorder. Electrical and other optional features may add $500-600, and packaging for use in hazardous or other particular environments may add an additional $3500.

ORGANIC LOADING

A number of parameters can be measured to evaluate organic loading. Most frequently used are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). For continuous on-line analysis, BOD is not applicable, as the usual test requires a 5-day incubation period, and attempts to produce BOD measurements rapidly have been unsuccessful. COD determinations require an acid digestion and normally require more than two hours in the laboratory. Neither of these parameters necessarily include all the carbon present, as some compounds may be resistant to biological and/or chemical oxidation under the conditions of the analysis.

Rapid techniques involving combustion of a sample have been developed. Carbon content can be found by measuring with an infrared analyzer the carbon dioxide produced during combustion. The fraction due to inorganic carbon is found by acid decomposition of another portion of the sample, followed by infrared detection. The difference in these values is assumed to be the total organic carbon (TOC).

Another combustion method uses a fuel cell to monitor the oxygen content of a carrier gas. Combustion of a sample produces a momentary oxygen decrease which is detected by the fuel cell. The TOD Analyzer manufactured by Ionics is of this type and is discussed in detail in Section III. Although this instrument has limitations, it is probably the most satisfactory on-line instrument available at present. It is priced at approximately $9000.

Another high-temperature instrument meters air into a sample, passes it into a furnace, condenses the gases, and measures oxygen remaining in the condensate. No user information is available on this instrument which is offered at $10,000 by Enviro Control, Inc.

Technicon Instruments states their AutoAnalyzer can perform COD analyses, but user information was not available.

The need for a continuous monitor of organic loading is apparently well-recognized by instrument manufacturers. Several companies have indicated that they are developing equipment for this purpose either by adapting a laboratory instrument or by producing a completely new design. There are many problems to be overcome, and the date at which any of these prospective instruments will become available is not known. Estimates range from "the near future" to "a year or so."

OXIDATION-REDUCTION POTENTIAL

A reversible oxidation-reduction electrode is one in which both oxidized and reduced states are present, each being convertible into the other by an infinitesimally small change of potential from the equilibrium value. In solutions a platinum electrode will acquire a definite potential dependent on the ratio of the oxidized to reduced form.

Oxidation-reduction potential (ORP) is used as a control parameter in the destruction of cyanides in wastewater, and possibly for other purposes. It can be measured with pH equipment by substitution of a platinum electrode for the glass membrane electrode. Some ORP electrodes incorporate an internal reference electrode. Most manufacturers of pH equipment can supply units with scales to read ORP in millivolts.

pH

The glass electrode or glass membrane for hydrogen ion sensing was developed in the thirties. Recently all components of the system have been greatly modified. The potentiometers have probably been changed the most; originally voluminous electrical units have been shrunken to miniature electronic devices.

While the glass electrode itself has been modified somewhat, the reference calomel electrode has been markedly redesigned and now even replaced. The need for frequent additions of salt solution in field use of the calomel cell led to larger reservoirs of saturated salt solutions in the salt bridge. Widely varying temperatures, however, under field conditions frequently caused crystal formation in the zone of the salt junction. The crystals caused breaks in the electrical continuity so that special maintenance was required. Recently three instrument companies have marketed a solid state reference electrode which eliminates the salt bridge problems by eliminating the calomel electrode. The solid state systems have been very successfully used in rugged chemical environments for recording and controlling pH.

Along with the modified electrodes, it is also possible to obtain an electrode assembly with a built-in preamplifier to permit signal transmission over distances up to a kilometer.

Small instrument companies are reducing the need for service personnel visits by using plug-in modules for pH amplifier-controllers. The need for a replacement can be ascertained by a description of the trouble over the phone and a duplicate modular unit shipped by express or the user company may keep a replacement module in stock for momentary replacement. The latter arrangement would seem wise in isolated situations or where many units were in service at one location.

Simple mechanically controlled pH controllers are generally available while electronically set controllers are available again in easily installed replaceable modules. In general, electronic accuracy for pH control is not needed for wastewater.

User replies have been received from 15 companies. Very few of the users have evaluated the equipment in wastewater and no further comment is considered necessary. Actually, pH instrumentation is so generally available that no need is seen to recommend a specific company. Many users have had unfortunate experiences with each of the larger companies, yet each company is capable of doing an adequate job.

For use in wastewater, a rugged electrode system is essential and preference should be given to a solid state reference cell. Preamplification of the signal at the electrodes should depend on the distance to the amplifier, recorder, controller equipment.

PHENOLS

Standard laboratory procedures for the colorimetric determination of phenols require either a steam distillation or solvent extraction. Alternately, a gas-liquid chromatographic analysis may be used. This more complex procedure requires more elaborate equipment, but may be used to identify specific phenolic compounds. This thin layer chromatography also has been used for the qualitative detection of phenols and as a separation technique for subsequent spectral identification.

One continuous on-line instrument for monitoring phenol was located. Manufactured by Teledyne Analytical Instruments for use in refinery effluents and elsewhere, it is a dual sample cell, split beam, chopper stabilized, photometric analyzer that measures phenol in a water composition by measuring the radiation absorbed in a selected band of the ultraviolet spectrum. The presence of small amounts of extraneous compounds such as oil, organic acids, sulfonates, and mineral salts constitutes a serious limitation to the determination by direct spectroscopic techniques of total phenol in refinery effluents. This limitation is circumvented largely by the application of differential absorbance measurements which utilize the spectral shift of the phenoxide ion in changing from acidic to basic solution. In practice, a dual cell ultraviolet analyzer is arranged to measure a portion of the spectrum centered around 2850A, where the phenol absorbs in basic solution but an acidic solution does not. If both cells are made acidic, the background level of oil, etc. is seen by both phototubes and is ratioed to zero reading. If one cell is then made basic, the characteristic phenoxide ion is seen by the phototube and its concentration may be recorded. The advantage of this method is that the background is continuously ratioed to zero, and the method is specific to phenol.

A sample preparation system is needed to eliminate the calcium and magnesium precipitate formed by the addition of caustic to salt water. The sample is mixed with sufficient caustic to cause a precipitate and make the sample strongly basic. The precipitate is separated by agitation in the stirring filter. The filtered sample is directed to the measuring cell in the analyzer, while the sample going to the reference cell is made acidic, and a differential measurement is made to record the phenol concentration present in the sample stream.

One user reported an unsuccessful trial of this instrument on a flow containing less than 5 ppm phenol in the presence of other ultraviolet absorbers. A major problem was to avoid interferences by obtaining an oil-free sample.

The Teledyne Analytical Instruments Phenol-in-Water System may be satisfactory for Air Force purposes, but insufficient user information is available on which to base a recommendation. The price of the system is $8600 plus $900 for a recorder. Optional electronic features would add $100-300.

The Technicon Instruments Company recommends their AutoAnalyzer equipment for phenol analysis, but no user information was supplied.

PHOSPHATE

The determination of phosphate is very important in wastewater, because phosphorus is essential to the growth of organisms and can be the nutrient that limits the growth which a body of water can support. Phosphates may be present in dissolved and/or particulate form, in readily determinable "orthophosphate" form, or in condensed form (pyro-, meta-, and polyphosphates). Condensed phosphate requires an acid hydrolysis to orthophosphate for determination. "Organic" or "organically bound" phosphate are the phosphate fractions which are converted to orthophosphate only by oxidative destruction of the organic matter present.

Laboratory analyses are made colorimetrically for orthophosphate. The conditions necessary to convert various fractions to orthophosphate define the forms in which it was initially present.

A continuous monitor is available from Hach Chemical Company which indicates orthophosphate. It was designed for use in boiler water and cooling towers where phosphates are used for corrosion and scale control. User responses were mixed and several indicated a need for preliminary filtration in order to provide a low turbidity sample. This instrument appears unlikely to provide satisfactory service in wastewater analysis.

Delta Scientific offers colorimetric analyzers for both orthophosphate and total phosphate, but no user information is yet available.

Technicon Instrument Company reports their AutoAnalyzer equipment is capable of both orthophosphate and total phosphorus analyses. No user information is available, but the need for high temperature digestion in total phosphorus analysis would seem to limit the utility of this instrument.

It is reported that Ionics, Incorporated will soon have an on-line orthophosphate analyzer available. It is designed for unattended operation and will perform five analyses per hour.

SILVER

The atomic absorption spectrophotometric method is generally preferred for silver determination. The colorimetric dithizone method is useful in the absence of atomic absorption equipment. Silver may also be measured by use of a spectograph or by neutron activation analysis.

A distinct possibility for continuous monitoring is a chemical sensing electrode specific for silver. See discussion of the Orion Series 1000 Monitor in Section III.

Delta Scientific reports the availability of a continuous spectrophotometric analyzer for silver, but no user information was available. The analyzer is priced about $3000.

SURFACTANTS

A great many substances normally found in wastewaters, effluents, and polluted waters interfere with the determination of surfactants, and in such liquids it is very difficult to obtain an accurate analysis. Laboratory procedures prescribed for the determination of anionic surfactants in water supplies may be used to establish concentrations in wastewater.

Linear alkylate sulfonate (LAS) is the most common surface active agent and reacts with methylene blue to form a blue-colored salt. Values obtained by this reaction consist of the true LAS value plus the sum of other interferences (usually positive). If the total concentration of methylene blue-active substances is low, no further analysis is usually required.

When the result is high or it is necessary to obtain more accurate results, an infrared determination can be made. In this method, a few milligrams of LAS is collected and isolated. Quantitative determination is then based on infrared absorption of an amine complex of LAS. Alternately, a colorimetric determination can be substituted by recovering the purified LAS and applying the methylene blue method.

No instrument designed specifically for either laboratory or continuous on-line monitoring of surfactants was located. Due to the complexities of the usual manual procedures, it does not appear likely that they could be successfully handled by automatic or semi-automatic devices. The only practical possibility for instrumentation appears to be in the discovery of a reaction that is specific for LAS, and one of whose products can be measured by an instrument.

SUSPENDED SOLIDS

Suspended solids in sludges and aeration-tank mixed liquors is determined in the laboratory by gravimetric methods. A special form of turbidimeter is available for continuous monitoring. See discussion under "Turbidity" in this report.

TEMPERATURE

Mercury-in-glass thermometers are the most widely used instruments for measurement of temperature. However, when a continuous written record is needed, other sensors are preferred. Thermocouples produce an electrical current proportional to temperature. Thermistors are electrical resistors whose resistance varies with temperature. Relatively simple electronic circuitry is needed with either of these types of sensors to indicate, transmit, or record temperature.

Extensive experience in measuring water temperature as well as inquiry elsewhere indicates no particular advantage for either type sensor when used with a proper electronic system. Installation should be arranged so that flow is not obstructed and the sensor does not become covered with matter preventing direct thermal contact with the liquid.

It is concluded that both thermocouple and thermistor systems are acceptable for wastewater monitoring.

TURBIDITY

Turbidity is not a narrow or closely defined concept. Rivers may have suspended clay: domestic wastewater has suspended organic matter and bacteria and each are turbid. Both the water and wastewater treatment plants have flocs that show turbidity. Originally turbidity implied suspended matter and/or colloidel matter that could develop a Tyndal cone in a light beam in a dark room. The reflecting particles may range in size from proteins a few nanometers in diameter to droplets of oil at fractions of a millimeter. As finely divided particles of clay or bacteria clump together the particles become suspended solids which may be measured with the same type of instruments. Concentrations may vary from less than a milligram per liter to several grams per liter.

Two different concepts are used in measuring turbidity. Ordinary colorimeters are frequently used to measure turbidity by light sorption. This technique requires the absence of color in the sample for any degree of accuracy unless a color blank is available. Because of the reflectance factor in a Tyndal beam, photocells can also measure reflectances by proper orientation of light source sample and cell where interference is blocked out.

Because continuous light favors algal growth on continuously submerged lighted surfaces including the light ports of a colorimeter, continuous on-line monitors have generally used the reflectance principle with both light source and photocells outside or above the sample. Recently matched photocells have been developed operating from a single light source. Now the submerged sensor can use two different length light paths so that the algal slime problem is overcome.

All turbidimetric instruments must be designed to specific concentration ranges. For very low turbidities a long light path is essential for accuracy. For high suspended solids a shorter light path or a different amplifier sensitivity may be used. With the light sorption instruments the range in turbidity requires different lengths of light path. For dispersion or reflectance instruments, a wide range in concentration of turbidity requires several amplifier ranges and may also have a different orientation of light to sample to photocell.

A major problem with turbidimeters whose light source strikes the water surface lies in the maintenance of a constant water surface elevation. Where the river or wastewater stream varies in elevation, pumps develop different pressures. The Honeywell river monitor turbidimeter uses back scatter light but is very sensitive to pressure variations, but works well with a source of water at constant pressure. A constant volume meter pump may be able to prevent sensor flooding which ruins the results.

A forward scatter matched cell submersible device is built by Monitor Technology with units to fit many ranges of suspended solids. It has been used successfully by the beer industry in the lowest range for controlling beer quality.

Nuclarus Limited produces a submersible light sorption system for "suspended solids." It has been widely used in Europe for both wastewater monitoring and treatment plant control. Various concentration ranges are determined with different heads. A common light source provides energy in two directions to photocells with different light paths. The differential light sorption is reported on an arbitrary scale; a standard is required for each range and one must be used each time a different probe is used. Long term use with a single range is claimed.

Hach Chemical Company produces a wide range of turbidimeters. Their low range turbidimeters are widely used in potable water plants and have proven quite satisfactory. Their surface scatter turbidimeter for the high range turbidities has several desirable design features; the light and photocells are removed several inches from the water surface.

None of the users contacted reported measuring the turbidity of wastewater. Most installations were in water treatment facilities where turbidity of finished water is very important and was being monitored. Satisfaction was indicated by all who responded.

ZINC

Zinc analyses may be carried out in the laboratory by atomic absorption or by the colorimetric dithizone or zincon methods. These colorimetric procedures are susceptible to many interferences and are used only when equipment for atomic absorption analysis is not available.

Polarography can also be used and is convenient as it may be applied simultaneously to a variety of metals. Present techniques permit sumultaneous determination of cadmium, copper, lead, nickel, and zinc.

No continuous or semi-continuous equipment for the analysis of zinc was located.

SECTION V

RECOMMENDATIONS FOR SAMPLING DEVICES

Water samples are collected and analyzed to ascertain characteristics of a larger mass of water. The sample is usually only an infinitesimal portion of the total, and can be truly representative only if the whole mass is uniform. If the characteristic of interest changes with time, the acquisition of an appropriate sample is more complex.

Waste flows typically fluctuate in volume and composition, and grab samples are of limited value as they represent the entire flow at only a single point in time. It is usually more satisfactory to obtain a sample that will reveal the average value over an extended period of time. There is no accord as to the best means of achieving this end and a wide variety of sampling devices is on the market. Most of them are at least moderately satisfactory for their design purpose, but may not function properly under other conditions.

Sampling liquids which contain appreciable amounts of suspended solids is particularly difficult, as solids tend to build up on wetted surfaces. This may interfere with the hydraulic and/or mechanical operation of the sampler.

It appears that the salvage value of worn-out or obsolete samplers would be quite low. Timers, motors, or other components might occasionally have use for other purposes, but otherwise the only residual value would be as scrap metal.

The Tru-Test Liquid Sampler is manufactured by Chicago Pump. A large capacity pump samples the stream and a portion of this is directed to a plenum chamber at the top of the sampler. Here, a motor-driven dip tube removes a sample at selected intervals and drops it into a gallon sample container which is kept in a refrigerated compartment. The sample motor may be run continuously or it can be controlled by a clock timer or by a flowmeter.

Satisfaction is reported by most users, but a high rate of corrosion of metal parts, particularly the dipper, was reported. Useful life of these samplers was estimated by several respondents to be 20-25 years. For collection of liquid samples under ordinary conditions in wastewater treatment plants the Chicago Tru-Test Sampler is recommended. For satisfactory operation (as indeed with any other sampler) it must be properly installed and receive regular cleaning and maintenance.

The current price of the refrigerated sampler is $2800-3000. Without the refrigeration unit it is $2300-2500.

The Sentinel Automatic Sewage Sampler offered by N-Con Systems Company, Inc. is similar in design to the Tru-Test Sampler of Chicago Pump. The case is constructed very substantially, and the refrigeration unit may be removed for servicing. It is priced at $2350 with the modular refrigeration unit. The non-refrigerated model is $1350.

Several manufacturers offer samplers which consist of a conveyor chain and bucket. The bucket is submerged at the bottom of its travel, and tips the filled bucket into a receiver as it reaches the top. This type of device can be readily adapted to lifts of almost any desired height by adjusting the bottom pulley or chain guide and length of the chain. Samples may usually be collected on a flow and/or time basis, and buckets of different sizes may be interchanged to regulate sample size. Refrigerated sample chambers are also available.

Phipps and Bird, Inc. manufacture a dipper-type sampler with an adjustable arrangement that allows the lower point of the dipper excursion to be as much as 10 feet below the base line. Users express satisfaction, but note that rags or large pieces of debris will jam the mechanism. The sampler with timer is priced at $635. In stainless steel it is $1145.

Model E Sampler of Quality Control Equipment Company is a similar device. The slim design allows it to be mounted through an 8 inch minimum diameter hole. The basic machine is $900. Several options are available including an all stainless steel version. All respondents to the questionnaire expressed satisfaction with this equipment.

BIF Sanitrol Series 40 and 41 Flo-Ratio Samplers operate on this principle. Several combinations of lift distance and material of construction are offered. User information was not available. Current prices range from $550 for minimum lift with fiberglass housing to $2600 for a stainless steel model.

The Trebler Sampler manufactured by Lakeside Equipment Corporation consists of a rotating scoop which gathers a sample representative of all depths of flow in a channel. The scoop is shaped so that the volume collected is proportional to the channel flow and the composite sample is proportional to the liquid flow. A time clock is available if continuous operation is not desired. The total volume passing the scoop can be estimated from a scoop calibration curve and an optional revolution counter. A refrigerator to hold collected samples is available.

Users express satisfaction with this sampler, although it must be used in conjunction with a Parshall flume or weir (90°, rectangular, Cipolletti). The scoop is narrow and must be cleaned regularly, particularly where suspended solids are high. The basic machine is priced at $750, and with a timer at $1100. The optional refrigerator is $600.

Isolok Automatic Liquid Samplers, Series M-4, manufactured by Bristol Engineering Company operate by forcing a plunger into the liquid. A sample is trapped when the plunger is withdrawn. The number of individual samples taken is adjusted according to time or by material flow to generate a representative composite sample. Individual samples are collected in a common container for subsequent analysis.

Although marketed primarily for sampling food and chemical process liquids, these samplers can also handle highly abrasive or viscous materials such as sewage sludge. A valve allows flushing of the interior surfaces as required. Users, including some sewage treatment plants, reported favorably on this sampler. A typical system including the sampler, mounting accessories, and controller is approximately $750.

Pro-Tech manufactures a line of liquid sampling equipment for various applications. Samplers are available in many configurations, including portable or fixed station, pressure or electrically operated, composite or discrete, timed or flow-proportional. Refrigerated and/or heated versions are available.

Pressure operated models collect samples by a metered gas flow into a surge chamber. When the preset pressure is reached, the gas is released to a remote sample chamber, submerged in the liquid, forcing the sample up to the sample bottle and blowing lines clear. For remote use, pressure is supplied by one-pound cans of refrigerant. Electrically operated models operate on a continuous-flow principle, and may be adjusted to collect either timed or flow-proportional samples. A model for obtaining discrete samples is also available.

Many users reported satisfaction, but a number reported frequent clogging of the liquid lines. It was noted by one user that the tubing absorbs oil from his sample stream, vitiating results. Another reported that lack of parts and information on the German-made refrigeration unit necessitated its replacement.

The pressure operated models are explosion-proof and could be considered for applications having this requirement. Prices range from $533 for a portable pressure operated sampler (Model CG-125) to $5600 for a stationary electrically operated device (Model DEL-2405).

Brailsford & Company, Inc. markets several portable effluent samplers. The Model DC-F is powered by a 6-volt battery which drives a small pump. The stroke of the pump is adjustable so that the volume of sample per stroke can be regulated. The pump operates continuously throughout the sampling period to collect liquid in a two gallon container. The current price of this sampler is $281 plus freight. Batteries are the major operating cost, but are reported to last about 30 days.

Brailsford Model DU-1 is similar to Model DC-F, but includes an electronic circuit which controls the pumping rate. An optional detector is available which makes the pumping rate proportional to water depth ahead of a weir. The price of the DU-1 is $325 plus freight.

Brailsford Model EV uses a vacuum pump to obtain samples, thus avoiding liquid contact with any pump mechanism or valves that could be clogged by an accumulation of material. Intervals between pumping cycles are adjustable. An optional detector regulates pumping rate relative to water depth ahead of a weir. Battery and line operated versions are available in the price range of $500-625.

Users of Brailsford samplers generally reported satisfaction. It was noted that the proportioning device operates on water level changes in one-inch increments, rather than continuously. It also requires a weir where flow is proportional to depth.

Sigmamotor, Inc. offers several models of automatic samplers for water pollution control. They are designed for portability, and most can be battery operated as well as by 115 volt AC. These samplers are nonproportional to flow, but timers allow wide variations in the sampling program and pumps are peristaltic tubing types. It is claimed that solids up to the size of the tubing will move freely to the sample container. Refrigerated versions are available.

Inquiries about these samplers revealed general satisfaction among users, but stoppage of the sample line by paper and other solids was reported. Other replies noted occasional failure of various parts of the system, and difficulty in obtaining spare parts in California. It is believed, however, that these samplers will provide adequate service under most conditions where proportionality to flow is not required.

Representative models and prices are as follows:
The Model WA-1, 115-volt AC composite sampler collects one sample of adjustable size every 30 minutes. It is priced at $400. With adjustable sampling frequency, $450. A refrigerated version, Model WA-2R is $700. For sampling streams with long fibers and larger particles, Sigmamotor suggests Model WA-4 at $700.

Model WM-2-24 is designed to collect 24 individual samples of 450 each. Sample frequency is adjustable on this $1200 device.

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

It is concluded that satisfactory instruments of proven reliability for continuous on-line monitoring exist for relatively few parameters: conductivity, dissolved oxygen, hydraulic loading, ORP, pH, residual chlorine, temperature, and turbidity.

For a large group of parameters some continuous or semi-continuous instrumentation is available. Much of this equipment is newly developed, and cannot yet be adequately judged. Certain available instruments perform in satisfactory fashion, but cannot be recommended for reasons such as high maintenance requirements or inadequate packaging for use in rugged field environments. Most of the shortcomings of instruments in this category are seemingly recognized by their manufacturers and presumably more satisfactory designs will evolve and inferior equipment will be eliminated.

A third group of parameters are those for which little or no instrumentation is marketed, and major research and development activity is needed. Also in this category are those parameters for which alternate types of instruments from those available might prove superior.

Only manual procedures are available for a fourth group of parameters such as filtrable solids, surfactants, and metals requiring atomic absorption spectrophotometry. In the future it may be possible to automate present procedures or to discover alternate methods of analysis more amenable to automation. Research and development activity is appropriate to parameters in this category, but should logically follow those in the third category unless unforseen events necessitate a change in priorities.

Table I is a general categorization of the parameters with which this investigation has been concerned. Some items fit into more than one class, and are listed in each. It is widely believed that all present equipment could be improved, and the availability of a satisfactory instrument does not necessarily preclude additional research and development.

It is apparent from the information gathered during this study that there is much activity in the field of wastewater instrumentation. The market place is crowded with sellers offering devices of both proven and unproven utility, and new vendors are appearing continually. Because of the state of flux that exists, a continuing surveillance of the market is strongly recommended.

Table I. Status of Continuous Monitors for Parameters of Wastewater.

a. Equipment available "off the shelf" with sufficient information to recommend use.

Chlorine residual	Oxidation-reduction potential
Conductivity	pH
Dissolved oxygen	Temperature
Hydraulic loading	Turbidity

b. Equipment available "off the shelf" but not recommended at this time.

Ammonia	Cyanide	Organic loading
Cadmium	Iron	Phenols
Chromium	Lead	Phosphate
Color	Nitrite	Silver
Copper	Nitrate	Suspended solids

c. Research and development required for continuous monitoring.

Color	Nickel
Cyanide	Nitrogen
Mercury	Organic loading

d. Manual lab procedures with automatic sampling recommended.

Cadmium	Oil and grease
Filtrable solids	Phenols
Lead	Surfactants
Nickel	Suspended solids
Nitrogen, Kjeldahl	Zinc

APPENDIX

EQUIPMENT SUPPLIERS

Automated Environmental Systems
Environmental Systems Center
Portsmouth, Rhode Island 02871

Beckman Instruments, Inc.
2500 Harbor Blvd.
Fullerton, California 92634

BIF Sanitrol
Unit of General Signal Corp.
P. O. Box 41
Largo, Florida 33540

Brailsford & Company, Inc.
670 Milton Road
Rye, New Jersey 10580

Bristol Engineering Company
204A South Bridge Street
Yorkville, Illinois 60560

Capital Controls Company
Advance Lane
Colmar, Pennsylvania 18915

Chicago Pump
622 Diversey Parkway
Chicago, Illinois 60614

Coleman Instruments
Div, Perkin Elmer Corporation
52 Madison Street
Maywood, Illinois 60153

Delta Scientific Corporation
120 E. Hoffman Avenue
Lindenhurst, New Jersey 11757

Enviro Control, Inc.
1250 Connecticut Ave.,N.W.
Washington, D. C. 20036

Fischer and Porter Company
7200 County Line Road
Warminster, Pennsylvania 18974

Hach Chemical Company
P. O. Box 907
Ames, Iowa 50010

Honeywell, Inc.
Industrial Division
1100 Virginia Drive
Fort Washington, Pennsylvania 19034

Hydrolab Corporation
P. O. Box 9406
6541 N. Lamar
Austin, Texas 78757

Ionics, Inc.
65 Grove Street
Watertown, Massachusetts

Lakeside Equipment Corporation
1022 E. Devon Avenue
Bartlett, Illinois 60103

Leeds & Northrup Company
Sumneytown Pike
N. Wales, Pennsylvania 19454

Monitor Technology, Inc.
303 Convention at Price
Redwood City, California 94063

N-Con Systems Co.,Inc.
Clean Waters Building
Larchmont, New York 10538

Nuclarus Limited
30 Fordhouse Blvd.
Toronto 18, Ontario, Canada

Olin Custom Analytical Instruments
120 Long Ridge Road
Stamford, Connecticut 06904

Orion Research
11 Blackstone Street
Cambridge, Massachusetts 02139

Phipps & Bird, Inc.
303 S. Sixth Street
Richmond, Virginia 23205

Pro-Tech, Inc.
Rogerts Lane
Malvern, Pennsylvania 19355

Quality Control Equipment Company
P. O. Box 2706
Des Moines, Iowa 50315

Schneider Instrument Company
8113 Camargo Road
Cincinnati, Ohio 45243

Sigmamotor, Inc.
14 Elizabeth Street
Middleport, New York 14105

Technicon Instruments Corporation
Tarrytown, New York, 10591

Teledyne Analytical Instruments
333 West Mission Drive
San Gabriel, California 91776

Union Carbide Corporation
Electronics Division
5 New Street
White Plains, New York 10601

Wallace and Tiernan
Div. of Pennwalt Corp.
25 Main Street
Belleville, New Jersey 01709

Weston and Stack, Inc.
446 Lancaster Avenue
Malvern, Pennsylvania 19355

Whitney-Montedoro
P. O. Box 1401
San Luis Obispo, California 93401

Yellow Springs Instrument Company
Yellow Springs, Ohio 45387