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INSTRUMENTAL ANALYSIS IN WASTEWATER TREATMENT

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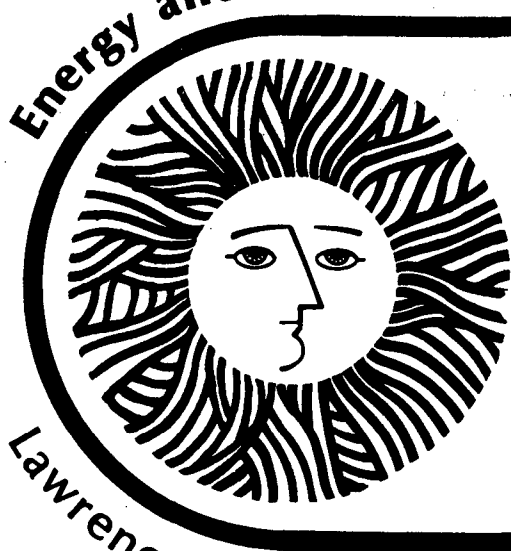
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Instrumental Analysis in Wastewater Treatment

Daniel A. McLean and Sidney L. Phillips

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Instrumental Analysis

in Wastewater Treatment

Daniel A. McLean
East Bay Municipal Utility District
P.O. Box 24055
Oakland, Calif. 94623

Sidney L. Phillips
Lawrence Berkeley Laboratory
University of California
Berkeley, Calif. 94720

Analytical chemistry is central to monitoring the operation of wastewater treatment systems. Its involvement began in the late 19th century with very rudimentary analyses and progressed to some of the most sophisticated analytical techniques currently available. This paper reviews briefly the development of wastewater treatment and the early analytical procedures used in the monitoring of these systems. The major focus, however, is on the application of instrumental techniques to wastewater treatment process control and effluent monitoring.

The practice of the collection, treatment, and disposal of human wastes has varied considerably over the course of history (1–4). Archeological evidence of sewers dates back to 3750 B.C. for the construction of a sewer at Nippur, India. The ancient sewers of Rome have been frequently described, and the sewer known as the *cloaca maxima,* constructed to drain the Roman Forum, still exists. However, these sewers were constructed primarily to provide storm water drainage. The discharge of human wastes to sewers was illegal until 1815, when London legalized the practice.

The early sewer systems only conveyed the untreated waste to local waterways. Treatment works were not constructed on a large scale until the 1860's, although chemical precipitation of wastewater had been practiced in England as early as 1762. The first large-scale treatment works were sand

filters, established in England in 1868. Biological treatment methods were also first established in England in the late nineteenth century. The now widely used activated sludge treatment system was developed in the United States in 1914.

The progress of wastewater treatment has accelerated rapidly in the last 60 years due to Federal and state requirements for higher levels of treatment. These requirements culminated in the passage of the 1972 Amendments to the Federal Water Pollution Control Act. Additional amendments passed in 1977 require secondary treatment for all municipal discharges by 1983.

Increases in the level of treatment required more sophisticated process monitoring to maintain efficient operation of treatment facilities. In addition, as treatment processes have become more complex, they have become more sensitive to the nature of the incoming wastewater. This has required increased monitoring of wastewater sources, particularly industrial discharges. Federal legislation has required the Environmental Protection Agency (EPA) and state and regional regulatory agencies to establish more and more stringent effluent quality limitations and receiving water quality criteria. These requirements increased the need for monitoring treatment plant discharges, receiving waters, and wastewater upstream of the treatment plant for constituents that are not normally removed in treatment.

The sophistication of analytical chemistry in the wastewater treatment field has paralleled the development of treatment methods and facilities. Early sanitary engineering and treatment plant operation was supported by analyses of the strength of the waste measured in terms of entrained solids and organic matter. Nutrients, primarily nitrogen and phosphorus, were of some interest. Physical parameters such as dissolved oxygen concentration and pH were important in consideration of corrosion of physical structures and operation of biological treatment systems. Control of sludge digestion processes relied on the analysis of pH, short chain fatty acids (volatile acids), alkalinity, and gas composition (methane and carbon dioxide). Treatment plant effluents were monitored for bacteriological quality as well as solids, organics, nutrients, and physical parameters.

Assessment of receiving water quality relied heavily on measurement of organic loading (BOD, COD) and bacteriological quality. Physical parameters such as pH, alkalinity, dissolved oxygen, and transparency (turbidity) were important in determining the effect of wastewater discharges and the effects of natural processes such as assimilation of nutrients by algae. Nutrients, primarily nitrogen and phosphorus, were important in evaluating eutrophic processes. In special cases, trace elements such as silicon, sulfur, and selected metals were determined at milligram/liter levels.

Table I. Classical Methods of Analysis

Constituent	Parameter	Method
Solids	Total solids	Gravimetric
	Volatile solids	
	Total suspended solids	
	Volatile suspended solids	
Organics	Biochemical oxygen demand (BOD)	Bioassay
	Chemical oxygen demand (COD)	Digestion, titration
	Volatile acids	Titrimetric
	Oil & grease	Gravimetric
Nutrients	N	Colorimetric, titrimetric
	P	Colorimetric
Physical	pH	Electrometric, titrimetric
	Alkalinity	Titrimetric
	Dissolved oxygen	Titrimetric
	Turbidity	Nephelometric, visual comparison
Digester gas	Methane	Orsat
	Carbon dioxide	Orsat
Bacteriological	Coliform bacteria	Multiple tube fermentation
Metals	Various metals	Colorimetric

Classical Methods

Early methods of analysis (Table I) were manual and what are now considered to be "classical": gravimetric, titrimetric, visual comparison, and rudimentary instrumental. The most significant early instrumental developments were the pH meter and the spectrophotometer. The routine use of spectrophotometers, in particular, allowed the development of more sensitive and specific methods of analysis for constituents of interest.

Other developments in instrumental methods of analysis also found use in the environmental field. Turbidimeters allowed more rapid and objective evaluation of the clarity of waters, especially the product of potable water treatment facilities, than visual comparators. The development of polarography in the 1920's was followed by the use of polarographic electrodes for the determination of dissolved oxygen. These electrodes were used for direct measurement of dissolved oxygen levels in environmental samples and were also applied to laboratory respirometer systems for determining the oxygen uptake of biological treatment systems. Polarography also found limited use in the analysis of heavy metals.

As analytical instrumentation became more reliable, these techniques were adapted to process control and field instrumentation. On-line pH meters were used in the influent to biological systems to warn of pH changes that might upset the process, in the control of chemical treatment of both potable and wastewater, and in the effluent from industrial processes to evaluate the effects of pretreatment and to ensure compliance with industrial waste regulations that were being developed by waste treatment agencies. Amperometric methods of analysis were applied to the determination of residual chlorine in both potable water and wastewater. Advances in nuclear chemistry, especially isotope separation techniques, were the basis of the development of nuclear density gauges for the measurement of solids concentrations in wastewater streams.

Modern Methods

At some point, one must draw a dividing line between application of "classical" and "modern" methods of analysis (Table II). The history of environmental analysis has varied from broad-based environmental assessment to concern with microenvironments and microconstituents. Based on the change in focus of environmental scientists, perhaps the best dividing line that can be drawn in terms of methods of analysis is with the development of atomic absorption spectrophotometry by Walsh in 1953 (5) and gas chromatography by James and Martin in 1952 (6). Prior to development of these instruments, analytical methods had been limited by both sensitivity and specificity.

The advent of atomic absorption spectrophotometry (AAS) and gas chromatography (GC) provided methods by which individual elements or compounds could be analyzed with high specificity and sensitivity. The success of these methods stimulated the development of instrumental methods applied to water pollution control.

Metals Analysis

The ability for rapid metals analysis at low concentration in samples that contained high levels of interference was a major boon to environmental scientists. One of the early issues to which AAS was applied was the extent of mercury contamination of biological, sediment, and water samples at microgram/liter levels. This analysis simply was not possible by classical methods.

Atomic absorption spectrophotometry has also found wide use in wastewater treatment facilities. The primary use has been determination of the metals concentrations in the influent to biological treatment processes to ensure that toxic metals do not upset the process. Metals found in the influent are traced upstream to industrial and domestic sources. Discharges from individual industries are monitored for compliance with discharge limitations established to protect the treatment process. Treatment plant effluent is monitored for heavy metals to ensure compliance with discharge limitations designed to protect the receiving water habitat and beneficial uses. Industrial discharges that do not pass through public treatment facilities are similarly monitored.

Thus, flame AAS has developed as a sensitive, specific, reliable, and widely used means for measuring the metal content of water samples.

Flame AAS, however, is subject to several limitations. The constituents of the sample matrix can interfere by reacting with atoms of the analyte in the flame. Since only free neutral atoms absorb light at the resonant wavelength, an error in the analysis occurs. Alternatively, the analyte atoms may be ionized in the flame and thus will not be detected. In cases where the metal content is below the instrumental sensitivity, a premeasurement concentration step is required. Another disadvantage is that only one metal can be determined at a time. Various techniques for dealing with these problems have been widely reported in the literature, and reviews have been published in this JOURNAL (7, 8).

Increasing interest in ultratrace concentrations of metals in the environment has resulted in the use of several techniques for enhancing the sensitivity of AAS analyses. Perhaps the best known are the various microsample devices consisting of various electrically or flame-heated boats, ribbons, cups, and furnaces (7, 8). By far,

the most popular has been the electrically heated graphite tube based on the original concept of L'Vov (9). The hot atomization method is more sensitive than the flame for many metals and is applicable in many cases to ambient concentration levels. Wastewaters that contain dissolved salts and solids attenuate light from the lamp by scattering due to smoke or salt particles produced during the heating steps. This requires background correction (9) using techniques such as recording the absorption of a nonresonant line from a hollow cathode lamp or continuum source.

Another method of analysis for metals which has found limited application to environmental samples is neutron activation analysis. This method has the advantage of determining many elements at once, of requiring little or no sample preparation, of measuring the total concentration of an element, regardless of its chemical state, and of being nondestructive. However, it is expensive and requires laborious radiochemical separation procedures to improve sensitivity and precision in some cases. Because of the size and cost of the facilities involved, the technique has been used primarily in research applications.

Polarography also deserves mention as a method of metals analysis. The technique was developed in the 1920's and has found use in some fields of analytical chemistry. However, it did not find wide acceptance in wastewater analysis primarily because complex formation made direct analysis difficult, and even with digested samples, the equipment was difficult to use. The technique was therefore limited in use to certain specific situations. New equipment, which will be discussed later, may make the technique more widely applicable.

Organic Analysis

At approximately the same time that trace metals became an issue in environmental concerns, scientists were beginning to look at the fate of organic compounds in the environment. One of the most widely discussed findings was the bioaccumulation of DDT and other chlorinated pesticides and their degradation products in widely varying types of animals. The study of trace organic compounds in the environment required the identification and quantitation of trace levels of a myriad of compounds in complex mixtures. Gas-liquid, and to a certain extent, gas-solid chromatography (GC) provided the means of analysis.

The first GC detector to achieve wide use was the thermal conductivity (TC) detector. The TC detector will respond to a wide variety of com-

Table II. Modern Methods of Analysis

Constituent	Method	Developing method	Comments on developing method
Metals	Flame and cold vapor, atomic absorption, colorimetry, AAS/graphite furnace, Zeeman effect AAS, polarography	ICP atomic emission spectrometry (AES), anodic stripping voltammetry, X-ray fluorescence	Multielement capability, less interference, multielement-increased sensitivity
NH_3	Colorimetry, automated colorimetry	Chemiluminescence, membrane electrode	
NO_3^-	Colorimetry, automated colorimetry, UV, ion-selective electrode	Laser Raman spectrometry	
PO_4^{-3}	Colorimetry, automated colorimetry	ICP emission spectrometry, ion chromatography, laser Raman spectrometry	Continuous field analyzers available
H_2S	Colorimetry, titrimetry	Membrane electrode automated titrimetry	Continuous analyzers
Cl_2	Colorimetry, titrimetry, continuous analyzer	Ion-selective electrode	Microcomputer available —
O_2	DO electrode	Continuous analyzer	
Pesticides	Gas chromatography	GC/MS, HPLC, NMR, GC/IR	Microcomputer available
Boron	Colorimetry	ICP–AES	5 g/L sensitivity with ICP–AES
Oxygen demand	BOD, TOC, COD	ICP–AES, TOD	TOC by ICP–AES
pH	Electrode	Continuous analyzer	Ultrasonic and other electrode cleaner available, transmitters to 3 miles distance
Turbidity	Turbidimetry	Continuous solids analyzer	Forward and backscattering instruments available
Temperature	Thermometer	Digital thermometer	
Coliform bacteria	Membrane filter	GC	Identification of metabolic by-products
Sludge digester gas, CH_4, CO_2	GC	Continuous analyzer, CH_4 detector	

pounds and is useful in fairly simple systems where the likely components are well enough known that compound identification may be made by matching the retention time of standards to unknown peaks in the chromatogram. One very useful analysis that relies on this detector is the analysis of methane and carbon dioxide in the gas produced by anaerobic digestion of sewage sludge.

Development of the flame ionization detector (FID) resulted in improved sensitivity relative to the TC detector, but very little change in specificity. The first real gains in specificity came with the advent of the electron capture (EC) and later the alkali flame (AF) detector. The sensitivity of the EC detector for halogenated compounds proved invaluable for analysis of the chlorinated pesticides and polychlorinated aromatics. When environmental pressures brought a decline in the use of chlorinated pesti-

cides and the organophosphorus compounds came into use, the AF detector was available as a phosphorus specific detector. The AF detector also has use in the analysis of nitrogen containing compounds. However, this detector had a reputation for being quite cantankerous and thus was rather restricted in its use. The later development of the Coulson (or Hall) detector for nitrogen and chlorine containing compounds and the flame photometric detector for phosphorus and sulfur compounds has increased the analyst's ability to thread his way through the bewildering array of organic compounds of environmental concern.

Along with developments in detectors, there have also been improvements in chromatography column technology and instrumental design. Both of these subjects are too complex to deal with here. Suffice to say, the column improvements of interest to the environmental scientist have in-

volved the improvement of solid supports to provide more stable materials and of stationary phases to provide better separation of structurally similar compounds. Instrumental improvements have primarily followed advances in the state-of-the-art of electronics. More will be said about this later.

Many wastewater treatment agencies and industrial dischargers routinely determine chlorinated hydrocarbons and PCB's in plant effluent using GC. The influent to wastewater treatment facilities may also be analyzed for toxic materials such as phenols that affect biological treatment processes. In addition, volatile organic compounds in treatment plant influents cause odor problems. The GC method is used to trace the odor-causing compounds to the source, to identify spills of various organic compounds into sewage systems and the open environment, and to identify and quantitate halogenated organic compounds, primarily those formed by the chlorination of water supplies and wastewater effluents.

In addition to identification of individual organic compounds, there are several gross measures of the concentration of organic substances in environmental samples. The most familiar of these, chemical oxygen demand (COD), total organic carbon (TOC), and total oxygen demand (TOD), are attempts to measure the potential oxygen demand of organic materials in a sample without the time constraints and inherent errors of the BOD determination. The COD method is little changed since it was first reported by Adeney and Dawson in 1926 (11), and thus really should be considered a classical method. The procedure has been automated (12), and numerous methods for reducing the time required for digesting the samples have been proposed (13), the latest being the use of a sealed ampule which allows the reaction to be carried out at elevated pressure as well as temperature (14).

The application of the total organic carbon determination to environmental samples was another attempt to measure the organic component of a sample that would yield definable and reproducible results. TOC relies on the oxidation of organic carbon in a sample to CO_2 (15). This is generally carried out in a furnace containing a catalyst through which a stream of oxygen is passed. Two techniques for detection of the CO_2 produced are in general use. The most common is a nondispersive infrared analyzer tuned to the major absorption band for CO_2. Alternatively, the CO_2 produced may be reduced to CH_4 and quantitated using a flame ionization detector.

TOC is specific for carbon. Hydrogen and nitrogen are converted to H_2O and N_2 and are not detected. Inorganic carbonates are converted to CO_2 at the elevated temperatures of the furnace and may be removed by acidifying the sample and sparging. In some instruments there are two channels, one of which oxidizes the sample at low temperature to determine inorganic carbon. The second column operates at high temperature to determine total carbon. Organic carbon is calculated by difference.

The third method of evaluating the organic content of a sample is TOD (16). In this procedure the sample is oxidized on a platinum or aluminum catalyst in a high-temperature furnace through which a stream of nitrogen containing a low partial pressure of oxygen is passed. The oxidation reduces the partial pressure of oxygen in the gas stream. This causes a change in the current in a fuel cell which is related to the concentration of oxygen demanding species in the sample. Quantitative results are obtained by standardizing the instrument against a known concentration of potassium hydrogen phthalate.

As the name implies, TOD measures the concentration of all components of the sample that will react with oxygen under the test conditions. Thus, inorganic species such as ammonia and sulfide as well as organic carbon and nitrogen will be determined. Nitrates and dissolved oxygen cause a negative interference by adding to the oxygen in the carrier gas.

On-Line Monitoring

On-line instruments are restricted to process control or monitoring situations. In-situ water quality analyzers will be discussed later. The applications discussed here are for water, wastewater, and industrial waste treatment.

The instrumental methods that have the longest term use in process monitoring are pH, conductivity, oxidation-reduction potential, dissolved oxygen, turbidity, and chlorine residual analyzers. The first three of these are simply industrial adaptations of well-known laboratory instruments. Bailey (17) has recently written a very complete description of the application of electrochemical sensors to process stream monitoring.

Dissolved oxygen (DO) is of great interest in wastewater treatment, primarily in biological treatment processes. All such methods rely on a biological culture for the assimilation of organic waste materials. The biomass in the system is then separated from the treatment process effluent and returned for additional duty or disposed (4). Since most of these processes are aerobic, control of the oxygen supplied to the system, usually by mechanical aeration, is important. Too little oxygen results in poor treatment efficiency, while too much wastes energy.

Dissolved oxygen concentration is also of interest in potable and natural waters. In both cases, lack of DO results in the establishment of anaerobic biological systems with the resultant production of foul tastes and odors. Thus, DO is regularly monitored in rivers, lakes, and marine environments to determine whether organic materials being added from industrial, domestic, or natural sources are causing biological activity that will exceed the capacity of the system to reaerate.

There are several instrumental methods for measurement of dissolved oxygen. An excellent discussion of these is found in a compendium of instrumental methods by analysis for environmental samples published by the Lawrence Berkeley Laboratory (18). The DO instrument in widest use is based upon the electrochemical determination of oxygen. Oxygen molecules diffuse across a semipermeable membrane, usually constructed of Teflon, and are reduced at the cathode of either a galvanic or polarographic cell. The Faradic current produced is linearly proportional to the concentration of dissolved oxygen in the sample cell. Both types of cells are used commercially, but the most common is the polarographic. The use of the membrane on the cell eliminates poisoning of the electrodes by constituents of the water that made prior use of electrochemical cells for direct field use impractical. The membrane electrodes must be equipped with a stirring device unless installed in a flow stream of fairly high velocity to maintain the concentration of oxygen atoms at the membrane surface. The primary problem experienced with membrane electrodes in on-line application is fouling or tearing of the membrane by materials in the stream. Membranes in wastewater treatment service tend to become fouled by attached microorganisms or grease. Some units are equipped with mechanical wipers to help remove these deposits. In some situations, other dissolved gases, such as hydrogen sulfide, may also diffuse through the membrane and react with the electrode, for example, the lead anode in a lead-silver electrode. All of the problems mentioned above make frequent standardization and maintenance of DO

Oxygen Demand Measurement
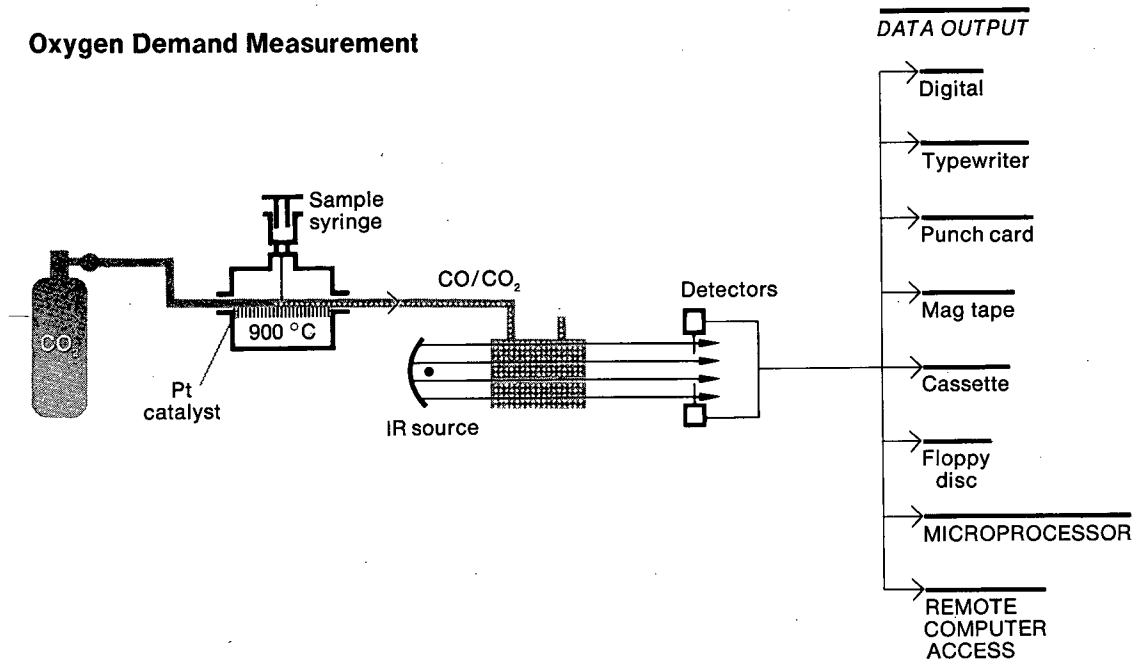
electrodes important. However, well-maintained systems can be used very successfully in on-line monitoring.

Turbidity relates to the appearance or clarity of a water sample and is the result of suspended matter. This is strictly a physical parameter and relies on the measurement of light scattered by suspended particles for determination. Turbidity is of interest in the evaluation of the effectiveness of filtration processes, especially in the treatment of domestic water supplies. Turbidity is important for both aesthetic and public health reasons. Suspended particles which cause turbidity can harbor bacteria and reduce the effectiveness of chlorination. The turbidity of natural waters is important because excessively turbid waters restrict light penetration which in turn cuts down on photosynthetic activity. Suspended particles which settle out can also block the interstices of rock and gravel bottoms, thus eliminating the habitat for certain aquatic organisms. Turbidity is of interest in industrial processes for the evaluation of product clarity. In wastewater treatment the turbidity of a process stream which is low in suspended solids may be related to the suspended solids concentration. However, this relationship is very particle-size dependent. Turbidity can be used to signal a process upset such as loss of solids from a clarifier or violation of an effluent suspended solids limit.

Since turbidity is a defined parameter, the test conditions must be defined. The measured turbidity is de-

pendent on particle size and on the wavelength of light incident on the sample. Thus, one must define the scattering angle and the wavelength characteristics of the source and detector. The current EPA accepted method (19) requires a 90° scattering angle. Because of the mechanics of light scattering in liquid suspensions, instruments with different design parameters will not necessarily give comparable results even though the same standard is used to standardize the instrument. Thus, the method of standardizing the instrument must be specified. R. D. Vanous (20) has recently published an interesting article on the necessary considerations in the design of turbidimeters.

Turbidimeters for on-line installation are of two general types: surface scatter and flow-through. In the surface scatter type of instrument, the sample flows into a constant level well. A light beam is directed at the surface of the light in the well, and the light scattered from particles near the surface of the liquid is measured at a specific angle from the incident light beam. This type of instrument has the advantage that there are no optical components in contact with the sample, and thus it is fairly easy to keep clean.

The second type of instrument is a flow-through unit in which the sample flows into and through a tube. Light is incident on the sample through an optical window located either on the side or end of the tube, and the scattered light is measured, again at a specific

angle to the incident light beam. Since there are optical components in contact with the sample in this type of instrument, it is necessary to provide a mechanical means of keeping the optical surfaces clean.

Both types of instruments may be standardized using a permanent standard. This is often a plastic cylinder containing a dispersed solid which, when inserted into the optical path of the instrument, will give a specific tubidity reading.

Perhaps the most widely used type of on-line analyzer in the water quality field is the chlorine residual analyzer. Chlorination of both potable water and wastewater effluents is widely practiced for the control of tastes, odors, and for disinfection. The analyzer is frequently linked to a control system for varying the chlorine dosage to maintain a specific residual in order to optimize disinfection or taste and odor control.

Current instruments are based on the amperometric determination of iodine formed by the reaction of chlorine with potassium iodide in a buffered solution (21). The sample supplied to the analyzer is diluted with a buffer whose pH is determined by the chlorine fraction that is desired to be determined and the sample is continuously pumped to the amperometric cell. The cell is composed of a platinum or gold anode and a copper cathode. Chlorine in the sample oxidizes the iodide in the buffer to iodine, and the amperometric cell responds to the concentration of iodine in solution.

Residual Chlorine Monitor
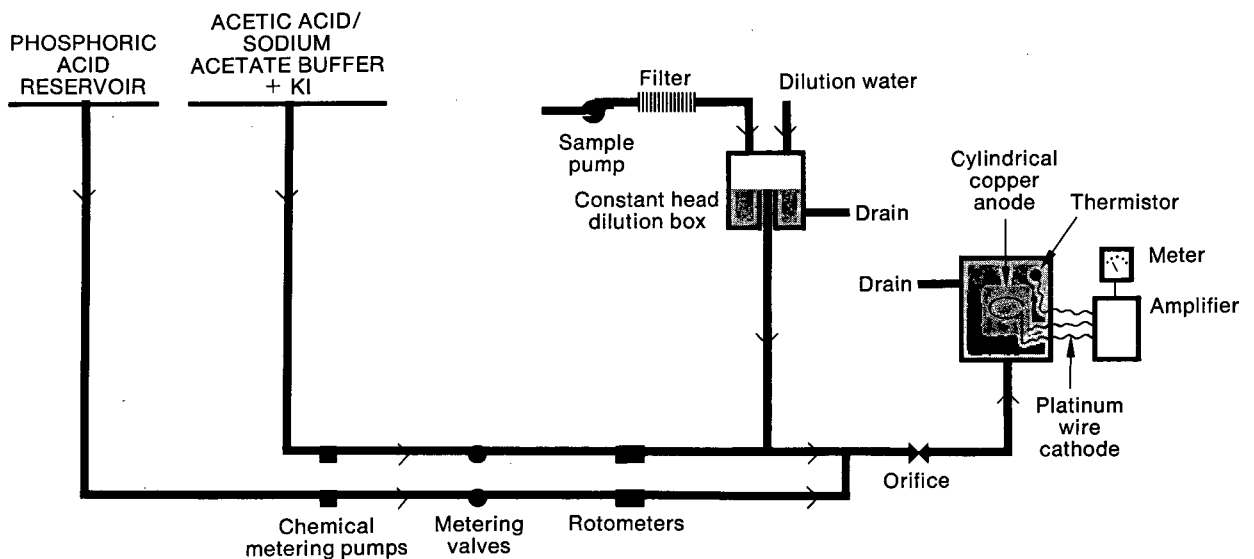
This signal is then amplified and displayed.

Depending on the constituents in the sample, applied chlorine may be present as "free available chlorine" or "combined chlorine." Free chlorine is present as hypochlorous acid or the hypochlorite ion. The combined chlorine fraction usually represents chlorine which has reacted with ammonia in the sample to form chloramines and, in wastewater samples in particular, may include chlorinated organic nitrogen compounds. Free chlorine is the best disinfecting agent with the chloramines being secondary. Chlorinated nitrogen compounds are generally ineffective in disinfection. Thus, according to the application, it may be desired to determine total chlorine, the sum of free chlorine and combined chlorine, free chlorine, or combined chlorine. This may be accomplished by varying the pH of the sample and depends on whether or not iodide ion is present. Total chlorine residual is generally the parameter of interest in wastewater treatment.

The amperometric method is relatively free of interferences, especially when total chlorine is being determined at pH 4. Iron, manganese, and nitrites, which are generally present in wastewaters, do not interfere. Other free halogens such as bromide and iodide will be oxidized and will cause positive interference. Silver and copper(I), present as the soluble cyanide ions, both poison the amperometric cell and thus interfere with the determination. Other problems that can occur in the use of residual analyzers are more mechanical than chemical, especially in wastewaters. Oils and greases in the sample coat sample lines and the electrodes. Control of pH is important and must be monitored, especially if the alkalinity of the water varies significantly. Iodide is frequently added to the buffer used to adjust the pH of the sample for convenience in addition to the analyzer. In this situation, iodide can be oxidized to iodine by oxygen and can cause a falsely high residual indication. This necessitates frequent recalibration of the instrument. In general, chlorine residual analyzers are very reliable instruments and are widely used in the water quality field (21).

In complex wastewater treatment plants, continuous monitoring of the organic load on the treatment process may be desired. Sophisticated control systems have made it possible to take signals from organic analyzers and apply the information to direct control of parameters such as aeration rate or flow-through biological treatment systems. Use of on-line instruments of this type allows optimization of process parameters for more stable operation of the treatment process and more consistent effluent quality. This type of control can also result in reduced power consumption for aeration equipment and internal pumping units.

The instruments used for this purpose are the total organic carbon, total oxygen demand, or chemical oxygen demand analyzers which have been described above. In general, process instruments are modifications of laboratory instruments to allow continuous sample flow to the analyzer, removal or size reduction of solids which might clog the analyzer, automatic injection of the sample into the analyzer, and display of the results. The results may be displayed on a local strip chart recorder, transmitted to a central control room, or input to a control system for direct control of the treatment process.

In general, the use of this type of instrumentation in on-line situations is not widespread. The analyzers frequently require maintenance and calibration at intervals which make them impractical for on-line use. In addition, the presence of oils, greases, and suspended particles in the wastewater may clog the instrument and can cause errors in the analysis. In cases where on-line instrumentation is used, direct control is very seldom practiced because of potential errors. Therefore, the general practice is to either perform frequent manual analyses or record the output of an on-line instrument and make adjustments to the treatment process as necessary.

Ion-Selective Electrodes

Designers of treatment plant monitoring and control systems tend to be conservative and rely on instruments which have been proven in the field over a number of years. However, specific ion electrodes have found some application in on-line monitoring for water and wastewater treatment plant

Turbidity Measurements

Side scattering

Front scattering

Polychromatic light

Back scattering
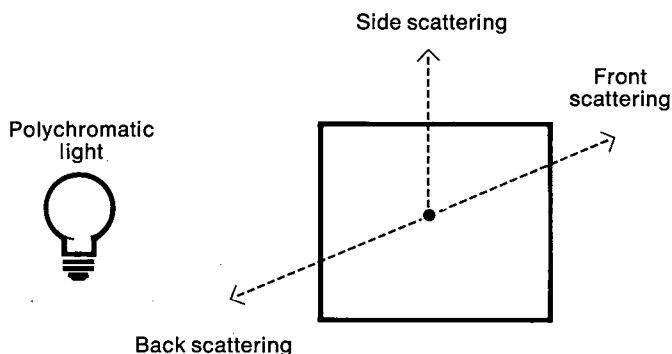
control even though the commercial application of these electrodes to on-line monitoring is fairly recent. Probably the most widespread application is the use of the fluoride electrode in the control of fluoridation of potable water supplies. The recently developed chloride electrode can be used as an alternative to the amperometric chlorine residual analyzer discussed above. The EPA, in many cases, requires dechlorination of chlorinated wastewaters before discharge. Sulfur dioxide is the usual dechlorinating agent. Sulfur dioxide specific ion electrodes are applicable to the control of sulfonation systems in dechlorination facilities. In areas where nutrient load on the receiving water is of concern, ammonia is frequently removed from wastewater by nitrification to nitrate. Ammonia specific ion electrodes can be used to monitor the effluent from nitrification plants. Cyanide and sulfide electrodes can be useful in monitoring influent to treatment plants where toxicity from industrial wastes can cause upset of biological treatment systems, or where odors generated by the incoming raw sewage may be a problem. In addition, these constituents may be monitored in treatment plant effluents to demonstrate compliance with effluent limitations.

Specific ion electrode-based process monitors generally suffer from the same problems as other on-line analyzers. The instruments tend to work well in potable water. Application to the analysis of industrial effluents of fairly constant composition can generally be worked out by proper treatment of the sample for interferences. However, the large number of potential interferences and the varying characteristics of wastewater create

sufficient problems for the instrument designer that application of specific ion-based monitors in this field has been limited.

The literature relating to the application of specific ion electrodes is extensive and has been reviewed recently by Buck (22).

Many other types of on-line analyzers are used in the water quality field, although not in great numbers. These are usually safety-oriented monitors and are often based on technology developed for other industries. Examples are hydrocarbon analyzers to determine potentially explosive conditions in sewer lines to which volatile chemicals may be discharged, and gas analyzers for the determination of the constituents of gas produced in anaerobic digestion of sewage sludge. A general review of the subject of on-line monitoring has recently been published in ref. 23.

Data generated from on-line monitoring instrumentation is generally handled in one of two ways. The analog signal from the monitoring device may be displayed and recorded. The device will usually have alarms to indicate variance of the process from certain limits. The recorded signal serves as a historical record and is used to make process control decisions. Alternatively, the signal from on-line analyzers may be input to a control loop for direct process control. In the past these controllers have generally been analog controllers. More recently, however, digital controllers have been used.

Receiving Water Monitoring

Most wastewater treatment plants discharge treated effluent into a re-

ceiving body of water. The need to monitor the receiving water to measure man's effect on the environment has long been recognized. This field of environmental monitoring has been increasing due to a growing awareness of the widespread effects of a single discharge. Much receiving water monitoring involves collecting samples in the field and returning them to the lab for analysis. The analytical techniques used are similar to those discussed above.

Increasing use is being made of in-situ monitoring of receiving waters. This type of monitoring is generally used for long-term studies of general receiving water conditions. Often the data are input to computer models which are used to predict the effect of an existing or proposed discharge under various meteorological or receiving water conditions. The instrumentation used is generally multiparameter. In addition, remote sensing using multispectral scanners and conducted from aircraft (24) or satellite platforms such as LANDSTAT or EROS is being developed (25).

The general requirements for in-situ monitoring instrumentation are the ability for long-term unattended operation, automatic calibration, and internal power and reagent sources. Frequently, control of the instrument package environment is necessary. The data output by the instruments may be recorded on strip charts, punch tape, or cassette tape, or may be telemetered to a central station.

Developing Technologies

Selected new instruments and techniques that appear most applicable to wastewater treatment will be discussed here. One of the most troublesome problems in routine AAS analysis has been the effect of nonspecific absorption (background) on the analysis. Two recent developments have approached the solution to this problem. In the first case, the Zeeman effect is applied to atomic absorption spectrophotometry (26). The radiation at the wavelength of the analytical line is split into two components—a nonresonant component and a resonant component. The nonresonant component is scattered by the background, whereas the resonant component is both absorbed by the analyte and scattered by the background. In many respects, this system operates similarly to the familiar continuum source background correction used in many atomic absorption instruments. However, it has the advantage of using a discrete wavelength close to the analytical wavelength to provide background correction virtually at the wavelength of measurement.

The second technique is the induction coupled plasma (ICP) atomic emission spectrometer (27, 35). In this method an induction coil is used to excite an electrodeless plasma discharge contained in an inert gas such as argon. Atoms have a long residence time within the plasma leading to a higher excitation probability and more intense signals. This high residence time accounts in part for increased sensitivity of the method compared to conventional AAS. The higher temperature of the plasma as compared to flame or flameless atomic absorption reduces many of the chemical interferences which are encountered in the other techniques. Since this is an emission type of determination, multielement capability is an additional attractive feature.

The gas chromatograph coupled to a mass spectrophotometer has been gaining increasing popularity in the analysis of trace organic materials in waters and wastewaters (28). This instrument is useful because of the increasing concern with trace organics in the environment, especially the problem of chlorinated organic compounds in drinking water supplies, and the relationship that chlorination of industrial and domestic effluents may have to this problem. The GC–mass spectrophotometer has the advantage over traditional chemical separation techniques in that the latter are too laborious and expensive and cannot always perform the necessary separations. The instrument has the disadvantage of being expensive and of requiring a computer accessible library to determine the identification of the mass spectra obtained. A variation of the GC–mass spectrometer is the infrared spectrophotometer coupled to a gas chromatograph. This type of instrument has been made more useful by the development of fast scan instruments, such as the Fourier transform spectrometer. Adaptations of computer data bases will no doubt increase the usefulness of this instrument.

High-pressure liquid chromatography (HPLC) (29) has developed as a useful adjunct to gas chromatography although it has not yet found wide application in wastewater analysis. The most common detector initially was an ultraviolet–visible spectrophotometer, although other detectors such as conductivity, amperometric and coulometric detectors are now being applied (30).

Polarography is not at all a new technique, but recent improvements in instrumentation have led to resurgence of interest in variations like anodic stripping voltammetry (31) for application to water quality analysis. The advantages of this technique are that it has multielement capability at

microgram/liter levels and the chemical state of an element may be determined. The primary disadvantage of the technique is that, for an element to be detected, it must be soluble in mercury.

X-ray fluorescence has found some application in water and wastewater analysis (32). The technique has the advantage of simultaneous multielement analysis for a wide range of metals and nonmetals with sensitivity to 0.1 mg/L. The primary disadvantages are the initial cost of the instrument and the necessity for considerable skill in the operation of the instrument and in the interpretation of the spectra. The technique also requires sample concentration when trace level elements are to be determined in aqueous samples.

Future Needs

Future needs in analytical instrumentation relate primarily to practical problems as opposed to research needs, and cover both laboratory and field problems. The general need is not for high-speed, high-volume instruments because treatment processes are physically large and respond within several minutes to a few hours to process changes, but rather for instruments which are highly reliable, specific for the constituent of interest, and as free as possible from interferences.

Classical analyses as defined in Table I can benefit from instrumental and automated methods. For example, the development of a solid state DO electrode which would do away with the problems of tearing and fouling of the membrane used with current electrodes would be a decided advantage. Improved pH electrode cleaning systems which minimize the problems of coating with substances such as hydrolized proteins or oils that inhibit the transfer of hydrogen ions at the glass membrane are needed as are reference electrodes that do not rely on ceramic or fiber junctions that become plugged. The recently developed gel-filled reference electrodes are an approach to the latter problem.

There is a definite need for quality assurance standards for various analyses. Standards already exist for many relatively stable constituents such as metals, nutrients, alkalinity, and turbidity, to name a few. However, there is a real need for standards for dissolved oxygen, suspended solids, chlorine, biochemical oxygen demand (BOD), and oil and grease. It would also be useful to have pH standards that contain some of the organic species that are present in wastewater and cause errors in the determination. Standards are available for some of this latter group of constituents, but

they are not composed of the compounds present in wastewater.

There is a real need for reliable solids analyzers, especially for low-level streams. There are currently instruments which are based on absorption of ultrasonic sound or on light scattering (34). The problem with these instruments is that they may be sensitive to particle size and/or density. Thus, it is necessary to develop the calibration between gravimetric solids analyses and instrumental values.

With biological treatment systems becoming more widespread, there is a requirement for a reliable on-line instrument which will relate to the bacterial respiration rate. Presently available instruments, in general, determine parameters that are only indirectly related to bacterial respiration.

Because of increasing monitoring requirements and the increasing cost of performing analyses, there is a need for small-batch wet chemical or colorimetric analyzers which can be used by small- and medium-sized laboratories for running batches of 10–20 samples. Currently available analyzers are generally too expensive, and the changeover from one analysis to another is too cumbersome to be of value in this situation. Instruments such as automated spectrophotometers, especially those equipped with sample changers, are a help to the beleaguered analyst. However, most of these systems require that the analysis be carried through to the final step manually before the sample is introduced to the sample changer.

There are certain needs that also apply to the list of modern analytical methods in Table II. In the case of trace metals analysis, the problems of background interference and lack of sensitivity for some elements are well known. These areas need additional study. In addition, there is a need for development of instrumental methods which will allow speciation of the elements of interest. In the case of nutrient analyses, instruments should increase the speed of the analysis and provide techniques which are free from interferences. Developments in this area could be applied to both on-line and laboratory-type instrumentation. In the field of trace organics analysis, the GC/MS may have the greatest applicability. The cost of these instruments has been decreasing; however, it is still beyond the range of many laboratories, especially considering the limited number of analyses which often are performed. The manufacturer here is obviously caught between the cost of developing instrumentation and the market that exists for it. However, a lower cost GC/MS instrument, perhaps with more limited data processing capabili-

ties, may find application. An alternative could be the further development of GC/IR instruments. Also, HPLC instruments may find greater applicability in the water quality field in the future. The main need for HPLC would be development of specific detectors similar to those available for gas chromatography. In general, instrumental developments which provide freedom from interference, less sample cleanup, and increased sensitivity are of general interest in the analysis of trace metals.

In the case of in-situ monitoring, the field may be divided into two broad areas: regional effects, that is, effects which influence an entire body of water and show the relationship between dischargers that are spatially separated; and local effects which are the effects in the receiving water in the immediate vicinity of a single discharge. The problems in the case of regional effects are primarily related to the gathering of large quantities of data over an extended period of time. This means that instrumentation applied in this field must be reliable enough to operate unattended for long periods of time. Recent developments in electronics have helped in this regard. In addition to the types of instruments currently available, it would be advantageous to develop analyses which could be related to the health of the biological community around the sampling station.

Currently, this is approached by gathering samples of the various organisms for identification and chemical studies. However, this procedure is extremely expensive and time consuming. Some indirect measure of the health of the biological system is needed. In some cases, it may be desirable to have remote monitoring equipment which can take profiles of the water column at the sampling location, rather than taking samples only at preselected depths. Except for the requirement for profiling, remote

monitoring from aircraft or satellites may be the best solution to these problems.

In the case of monitoring local effects, data from several sample stations are required, and profiling of the water column is highly desirable. In this case, unattended operation is often not a requirement, since the sampling stations are generally not physically remote from the treatment facility. Here again, there is a need for parameters which will relate to the health of the biological community. There is also a need for data management systems for the monitoring devices used for local effects work. These data systems are especially important if the data gathered are to be input to a water quality model. Developments which increase the reliability of the sensors or decrease interferences will increase the applicability of this type of instrumentation. In addition, instruments which would be capable of in-situ monitoring of nutrients such as nitrogen, phosphorus, and carbon would be an advantage.

The foregoing discussion shows that the skills of the analytical chemist have become as important to the proper operation of modern wastewater treatment facilities as are the skills of the engineer in designing the plant and the operator in operating the plant. Analytical chemistry is involved in the full range of environmental assessment from the initial study of relationships in the environment and the impact of man's activities on those relationships, to the support of pilot-scale studies of treatment processes to mitigate those impacts, to the evaluation of the effectiveness of full-scale treatment facilities. It will be necessary for the analytical chemist engaged in the support of operation of wastewater treatment facilities to continue increasing his expertise in the field and to use the most modern and sensitive methods of chemical analysis available.

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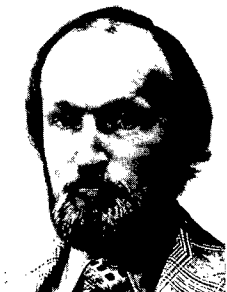
Daniel A. McLean is laboratory supervisor at the East Bay Municipal Utility District Water Pollution Control Laboratory. His professional interests are in the development of analytical methods for process control and environmental monitoring.

Sidney L. Phillips is principal investigator of aqueous electrolyte energy properties at the Lawrence Berkeley Laboratories. His research interests are in analytical chemistry and computer storage of basic energy data.

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LAWRENCE BERKELEY LABORATORY
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