INSTRUMENTAL ANALYSIS FOR WATER POLLUTION CONTROL

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I - INTRODUCTION

A - Chemical Analysis For Water Pollution Control

The seriousness of the problem of water pollition and its impact on environmental health is presently under the focus of international attention. Never was there a time in the history of man when he was so deeply concerned with the quality of his water. Much legislation has been passed and appropriations have been made to restore the quality of man's environment. The chemical industry, accused of being a main contributor to pollution, is undertaking expensive programs designed to limit emmission and improve disposal of industrial wastes as well as to assure fitness and appropriateness in the use of industrial products.

The analytical chemist, as a member of a team conbining various disciplines such as other scientists, engineers, lawyers, sociologists, physicians, and economists, plays a significant role in the total effort of water pollution control. His role requires him to characterize the nature and magnitude of the problem, assist in executing a control measure or treatment process, and last but not least, provides a continuous surveillance and monitoring of the final product, i.e. clean water. To this effect the analytical chemist is the "eyes" and "ears" of any control measure - for without valid, meaningful analysis our efforts to control pollution will be fruitless.

There was a time when all that water analysis did consisted of simple titrimetric and gravimetric procedures. Nowadays, with the obvious increase in the magnitude and the ways by which man is polluting his waters, there is an ever broadening need for more accurate and precise information on water quality. The determination of a specific element or compound in a water sample frequently requires extensive separation work to remove interferring constituents before identification and quantitative measurements

can be performed. All too frequently, this is followed by one or multiple identification procedures which may involve the use of such sophisticated equipment as emmission and absorption spectrometry, mass spectroscopy, NMR, X-ray, thermochemical and electrochemical techniques. For example, the analysis for certain organic compounds in river waters requires, at first, concentration by adsorption on carbon columns, or partial freezing or reverse osmosis membrane techniques. This is followed by separation with liquid-liquid extraction, gas-liquid chromatography, or thin-layer chromatographic techniques and finally, the identification and measurement are done by infrared spectrophotometry.

B - What Is Unique About Water Analysis?

The chemical analysis of natural and waste waters is one of the most challenging tasks that is likely to confront any analytical chemist. The test solution is, in most cases, a complicated heterogeneous system that rarely lends itself to simple analytical techniques. "Water" analysis not only requires the subtle correlation of theory and experience of analytical principles, but also a keen insight into the nature of interferences and other problems associated with the methodology. Interferences may be quite unique to a particular water system and in many ways yield inaccurate data and cause misleading conclusions to be drawn. Water analysis requires the ability to properly interpret analytical results in correlation to pertinent field observation and the history of the water.

Water pollution control can be looked at as a specialized technology and, like any other industry, it has its own specific analytical needs. Analysis may be required to (a) determine the compliance of certain waters or waste waters with quality standards for an intended use, production control or disposal in a receiving stream; (b) estimation of possible

detrimental effects waste effluents on the quality of a receiving water for subsequent downstream use and (c) evaluation of treatment requirements in view of water reuse.

Some of the more unique analytical parameters characteristic of the water pollution control industry are the BOD (biochemical oxygen demand), COD (chemical oxygen demand), taste, odor, color, chlorine demand, hardness, alkalinity, bioassay using fish or crustaceae and biodegradability tests. The analytical chemist, experienced in water quality characterization, can decide based on practical intuition, on what parameter and test to use for a given purpose of analysis.

Perhaps the most challenging and most meaningful type of analysis for water quality characterization is that which involves in situ measurements. This technique is preferred over analytical procedures which involve removal of the water from its natural environment, in the form of "grab" samples or in the form of a continuous flow stream, for subsequent analysis in the laboratory or field station. The main disadvantage of the latter procedure can be related to the problem of collecting samples which, in most cases, cannot be done in such fashion as to give a true representation of the test solution, and to the fact that the analyses are usually performed under environmental conditions quite different from those which existed at the sampling site. For example, changes in pressure and temperature may result in the escape of gases with consequent occurrence of chemical or biological transformations of the species under test. In monitoring water quality, the grab sample methods not only lacks required statistical accuracy, but also can be relatively expensive on a cost per sample basis.

Before the instrumentation era, a classical method of the in situ analysis for toxic compounds in water was based on the survival of mosquito

fish. In a fashion similar to the 19th century practice of using canaries to detect the presence of toxic gases in coal mines, "Bumbosia affinis" has been used to monitor industrial waste effluents. Although this method lacks specificity, yet bioassay techniques, using various biological indicators, are inherent methods of water quality characterization.

Certain parameters easily lend themselves to in situ measurements such as temperature, turbidity, pH, and salinity. Electrochemical techniques, in general, are suited for in situ measurements. The effect of interferences, due to the presence of electroactive as well as surface active species in the test solution, can be minimized by covering the indicator electrode with permselective membranes. Examples of such systems are the voltammetric membrane electrode systems used for the in situ measurements for dissolved oxygen or certain metal ions. Potentiometric membrane electrode systems using glass or crystal membranes have been also used for measurements of specifications and anions.

C - What Are The Responsibilities of The Water Analyst?

In the water pollution control field the analytical chemist is expected not just to prescribe a workable procedure, but also he is asked to optimize the technique in order to reduce the time and effort required to obtain the needed information. Besides his responsibility for chemical analysis, a good part of his efforts is devoted to the diagnosis of problems, definition of analytical needs, design of measurement systems and development of a master plan of how to report, evaluate and integrate information with that of other efforts on the same problem.

Unlike other chemist, the water analyst has to be able to work with other professional groups such as engineers, physicians, aquatic biologists, lawyers, etc., and non-professional citizen groups on the local, state, and

federal levels. He is frequently faced with all kinds of questions that may have nothing to do with analysis and must make decisions and recommend actions on the spot. Based on his ability and initiative the job of the water analyst can be most challenging as well as rewarding.

II - DESIGN OF MEASUREMENT OF SYSTEMS

A - Objectives Of Analysis

Definition of the purpose and objectives of analysis is the first step in the design of any measurement system; this includes the definftion of particular problems to which solutions are sought. Some of the more common objectives of industrial wastwater analysis are as follows:

a) estimation of possible detrimental effects of the waste effluent on the quality of a receiving water for subsequent downstream use;

b) determination of the compliance of the wastewater with quality standards for water reuse, production control, or disposal in municipal sewers;

c) evaluation of treatment requirements in view of water reuse; and

d) recovery of valuable by-products from the waste effluent.

Natural bodies of fresh water can be classified according to intended use, including; public water supply, fish or shell-fish propogation, recreation, agricultural use, industrial water supply,hydroelectric power, navigation, and disposal of sewage and industrial wastes. Under the terms of the 1965 Water Quality Act in the U.S.A., industries which discharge liquid waste directly or indirectly to receiving waters are obligated by Federal law to conform to specific water quality criteria or standards, set by local and state agencies and approved by the Federal Water Pollution Control Administration.

Methods for implementing and enforcing compliance to water quality standards vary from one state to another. Quality criteria may be established for receiving waters into which wastes are discharged; such criteria are termed "stream standards." A second method for controlling quality of receiving waters is that of setting quality standards on the effluent itself. Conservation and Public Health agencies in general favor the so-called

"effluent standards." Conversely, industry in general prefers establishment of stream standards, since effluent standards most often do not provide for full use of the capacity of streams for assimilation of wastes.

Chemical analyses associated with control and treatment of industrial wastewaters for purposes of conforming to standards of water quality for streams, lakes, ocean outfalls, or underground aquifers, are often more complicated than those required in instances where the standards are set for the waste effluent itself; indeed, the respective methods of analysis and interpretation may be quite different in these two cases. In the former case the analysis is directed not only to characterization of the quality of the waste effluent but also to determination of its effect on the ecosystem of the receiving water, while in the latter case the quality of the specific waste is the only matter of concern.

Quality standards on industrial waste effluents vary from one place to another and are primarily dependent on whether the effluent is disposed of into a natural body of water (i.e., river, lake, ocean) or into a municipal sewage treatment plant.

One common method for estimation of the deleterious effects a waste effluent will have on the quality of a receiving water is to treat the wastewater as a complete entity, thus avoiding analyses for particular constituents. For this type of evaluation the wastewater is first diluted to a level corresponding to that which would occur in the receiving water and then certain gross parameters, such as taste, odor, color, and toxicity to fish, are measured depending on the intended water use. While this procedure may give a preliminary indication of the ability of the waste to be assimilated harmlessly in the receiving water, its effectiveness for providing sufficient basis for any significant conclusion is highly doubtful.

Among other things, the rate of self-purification of the receiving water is not accounted for in such a test procedure. Self-purification of streams and other receiving waters is a dynamic process involving a multitude of physical, chemical and biological reactions, the rates of biochemical transformation of pollutants are often much more significant than the ultimate assimilative capacity of the stream per se. For example, in evaluating the biochemical oxidation demand (BOD) of a particular waste water, determination of the rate constant is at least as important as determination of the five-day BOD. This mehtod of analysis will be discussed in detail in a later section of chapter.

The analysis of wastewaters which are to be discharged to municipal sewers is done principally for the purpose of evaluating compliance with certain effluent criteria set by the municipality. Effluent standards in this case are established for the purpose of protecting municipal waste treatment plants from operational interference which might be caused by industrial waste discharged and for protection of the sewer structure from damage. Both the municipality and the industry may carry out periodic analysis of the waste effluent for purposes of control and assessment of charges, which are usually related to the strength and volume of a particular waste. It is important to point out that waste water which is discharged to municipal sewers usually becomes the responsibility of the municipality. The general requirements for acceptable wastewater for joint treatment with municipal wastes have been discussed in some detail by Byrd and others.

As far as in-plant operations are concerned chemical analysis of industrial wastewaters are preformed for one or more of the following purposes:

a) estimation of material balances for processes to permit evaluation of unit efficiencies and to relate material losses to production operations;

b) evaluation of continuing conformance to limits set for performance efficiency of certain unit processes;

c) evaluation of the effectiveness of in-plant processes, modifications and other measures taken for reduction of losses;

d) determination of sources and temporal distributions of waste loads for purposes of by-product recovery or segregation of flows, relative to strength and type, for separate treatment;

e) provision for immediate recognition of malfunctions, accidents, spills or other process disturbances;

f) determination of the type and degree of treatment required for recovery of certain substances from waste effluents;

g) evaluation of conformance to standards set for effluent quality and/or stream quality;

h) provision for control of treatment and discharge of waste effluents according to present standards and/or according to variations in the conditions of the receiving water; and

k) provision of a current record of costs associated with discharge of waste effluents to municipal sewers when such costs are at least partially based on the chemical characteristics of the waste.

Some of the objectives of industrial wastewater analysis listed above are of course exploratory in nature and therefore occassional in frequency, while others are related to continuous or regular monitoring and control.

B. CHOICE OF PARAMETERS FOR ANALYSIS

After defining the objectives of analysis, the next step in the design of measurement systems is to decide on particular constituents for which analyses are to be made and what methods are to be employed. The analyst experienced in water quality characterization can often make the proper decision based on practiced intuition. In most cases, however, certain rather well defined guidelines should be followed.

Depending on the intended subsequent use of a receiving water, the parameters listed in Table II-1 are of significance for water quality characterization, and this should serve as guidelines for analysis of wastewater quality for purposes of treatment and control.

The choice of parameters for analysis depends primarily on the type of information sought. Certain tests are frequently used for the identification of various types of pollution associated with industrial wastewaters. Table II-2 lists a number of tests and their significance.

C. CHOICE OF METHODS OF ANALYSIS

Choice of methods of analysis should be based on familiarity with the purpose of analysis, and on the origin, properties, and

TABLE II-1 PARAMETERS FOR WATER QUALITY CHARACTERIZATION

Water Use	Quality Parameters
Domestic Water Supply	1. Color, odor, taste. 2. Organic Content: chlorine demand COD, BOD, TOC, phenols. 3. Carcinogens and toxic compounds, insecticides, pesticides, detergents. 4. Turbidity, salinity. 5. Alkalinity, pH. 6. Total Hardness, Ca, Mg, Fe, Si, etc. 7. Pathogenic organisms, total bacterial count ($37^{o}C$), *E. coli* count, plankton count.
Fish, Shellfish, Wildlife and Recreation	1. Color, odor. 2. Toxic compounds 3. Turbidity, floating matter, sludge deposits, salinity. 4. Temperature. 5. Dissolved oxygen, BOD. 6. Alkalinity, pH. 7. Pathogenic organisms, plankton count.

TABLE II-1 (cont.)

Water Use	Quality Parameters
(continued)	8. Nitrogen, phosphorous, etc. (inorganic nutrients which support algae blooms and other undesirable aquatic growth).
Agricultural Irrigation	1. Salinity and Na-Ca content. 2. Alkalinity, pH. 3. Pesticides, growth regulators, etc. 4. Persistent synthetic chemicals (e.g., polyethylene derivatives, asphalt sprays, etc.). 5. Pathogenic organisms.
Watering of Livestock	1. Salinity. 2. Toxic compounds. 3. Pathogenic organisms. 4. Plankton count

TABLE II-2 SIGNIFICANCE OF PARAMETRIC MEASUREMENTS

Test or Determination	Significance
Dissolved Solids	Soluble salts may affect aquatic life or future use of water for domestic or agricultural purposes.
Ammonia, Nitrites, Nitrates, and Total Organic Nitrogen	Degree of stabilization (oxidation) or organic nitrogenous matter.
Metals	Toxic Pollution
Cyanide	Toxic Pollution
Phenols	Toxic Pollution, odor, and taste
Sulfides	Toxic Pollution, odor
Sulfates	May affect corrosion of concrete, possible biochemical reduction to sulfides
Calcium and Magnesium	Hardness
Synthetic detergents	Froth, toxic pollution

intended future use of the water under test. Some of the factors regarding informational requirements that should be considered in establishing methods of analysis are: (a) the required degree of sensitivity and accuracy; (b) the required frequency of analysis; and (c) the relative desirability of field and laboratory analysis.

Another point for consideration in selecting analytical methods concerns the collection, transportation and storage of samples. Screening tests should be conducted for purposes of approximating required sample volumes, establishing desirable sites for and frequency of sampling, and providing a rough estimate of the waste composition and strength.

Listings of "standard" and "recommended" methods for analysis of natural waters and wastewaters are to be found in a variety of publications sponsored by several water works, pollution control, and public health agencies and organizations in this country and abroad. In addition, in several instances certain private industries have found it desirable to formalize listings of more specific methods for analysis of particular types of industrial wastewater.

While general procedures of analysis for specific waste constituents are highly useful, the industrial-wastewater analyst must be careful to guard against over-reliance upon such procedures, and against the possibility of being lulled into a false sense of security by results obtained from application of such procedures in instances where they may not be applicable. Indiscriminate application of general-purpose methods for analysis without due

consideration of specific interferences and other problems must be avoided. Standardization upon procedures should be made only after these procedures have been thoroughly evaluated in terms of particular analytical requirements. Continuing use of such standard methods without modification should then be subject to the condition that the characteristics of the waste being analyzed do not change significantly over the duration of the analytical program. Just as the skilled medical doctor will not prescribe treatment or medication until he has carefully examined the patient *in toto*, so the analytical chemist should select his approach to the analysis of an industrial wastewater only after making a careful diagnosis of the total problem. This diagnosis should include consideration of: (a) objectives of the analysis; (b) requirements of speed, frequency, accuracy, and precision of analysis; (c) effects of interferences; and (d) effects of systematic and environmental conditions on sampling and measurements; etc.

III. DESIGN OF SAMPLING PROGRAMS

The chemist must, in addition to analyzing samples, participate in the design of sampling programs, and interpret and report the analytical results in a manner usable to others. The purposes of this chapter are to describe statistical methods used in the analysis of data, factors in the design of a sampling program, methods of sample collection and storage, and the collection of correllary field data.

A. Statistical Analysis

Statistical analysis is used routinely in the determination of the precision of a method, but also can be used in the comparison of means and precisions of sets of data, in fitting equations to experimental data, and in designing experiments. Errors are of two types, systematic and random. Systematic errors are unidirectional and therefore will affect the accuracy of a determination. The precision obtained may be high in a method which has a systematic error, so that one should realize that high precision does not imply high accuracy. Systematic errors can be assigned to definite causes and will always be of the same sign. The magnitude of the error may be constant, proportional to the amount or concentration of some constituent, or vary in some more complex manner. Systematic errors can arise from the incorrect preparation of a standard solution, not correcting for the solubility of a precipitate, or not removing suspended matter from samples prior to colorimetric analysis.

Ramdom errors are a result of uncontrollable factors. Ramdom errors are as likely to produce a high as a low result, but small errors will be more likely than large ones. Precision relates to the reproducibility of a measurement; accuracy is the nearness of the result to the true value. Ramdom errors reduce reproducibility, but by making sufficient measurements accuracy may not be affected. A systematic error will affect the accuracy but may or may not affect precision.

The standard deviation (s or σ) of a series of measurements

is a statistic which measures the scatter of the values and, therefore, is a measure of precision. The standard deviation may be calculated by the equation

$$s = \left\{ \sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n - 1} \right\}^{1/2} \qquad \text{(III-1)}$$

where n is the number of observations, x is a measured value, and $\bar{x}$ is the average of all observations. Another form of the equation is much simpler to apply when using a calculator or computer.

$$s^2 = \frac{1}{n - 1} \left\{ \sum_{i=1}^{n} x_i^2 - \frac{(\Sigma x_i)^2}{n} \right\} \qquad \text{(III-2)}$$

In this equation the average is not needed for the computation.

The true mean for a population, μ, may be estimated from the experimental mean, $\bar{x}$, of n samples with a standard deviation s.

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} \qquad \text{(III-3)}$$

The value of t for γ degrees of freedom ($\gamma = n-1$) is given in standard statistical tables for various confidence levels. In most cases the 95% or 99% confidence level is used in the estimation of the range in which the true average lies.

Linear calibration curves are often used for analyses by colorimetric and other instrumental methods. The data are plotted with the dependent variable, instrument response, as the ordinate and the independent variable, concentration, as the abscissa. If a straight line is fitted by inspection the greatest emphasis will usually be placed on the samples containing the highest and lowest concentrations. These values are often the least accurate. The slope and intercept of the best line through

the experimental values are determined by the least squares analysis. In this analysis the sum of the squares of the deviations of the experimental values from those calculated by the method of least squares are minimized. The analysis requires the computation of Σx_i, Σy_i, Σx_i^2, and $\Sigma x_i y_i$. The equations for calculating the slope, m, and the intercept, b, of the line $y = mx + b$ are

$$m = \frac{n\Sigma x_i y_i - \Sigma x_i \Sigma y_i}{n\Sigma x_i^2 - (\Sigma x_i)^2} \qquad \text{(III-4)}$$

$$b = \frac{\Sigma x_i^2 \Sigma y_i - \Sigma x_i \Sigma x_i y_i}{n\Sigma x_i^2 - (\Sigma x_i)^2} \qquad \text{(III-5)}$$

where the summations are carried out for observation 1 through observation n. The denominators of both equations are the same. An example of a least squares analysis for a calibration curve for the determination of iron by the phenanthroline method is given in Table 1.

Table III-1. LEAST SQUARES ANALYSIS OF COLORIMETRIC STANDARD SERIES DATA

Concentration (X)	Absorbance (Y)	X^2	XY
0.0	.005	.00	0.0000
0.4	.068	.16	.0272
0.8	.135	.64	.1080
1.2	.201	1.44	.2412
1.6	.260	2.56	.4160
2.0	.325	4.00	.6500
6.0	.994	8.80	1.4424

$$m = \frac{6(1.4424) - 6.0(0.994)}{6(8.80) - (6.0)^2} = \frac{2.7904}{16.80} = 0.16609$$

$$b = \frac{8.8(0.994) - 6.0(1.4424)}{6(8.80) - (6.0)^2} = \frac{0.0928}{16.80} = 0.005523$$

Statistical tests may be used to give a yes or no answer regarding the significance of data. The answer is obtained at some confidence level which indicates the certainty of the answer. The analyst must use his judgement in selecting the confidence level. If too high a level is selected, significantly different data will be judged the same, but if too low a level is selected, insignificant differences will be judged to be significant.

The t test is used to test the hypothesis that two means do not significantly differ. The test is useful for the comparison of results obtained by two different methods of analysis or by two analysts. Many modifications of the test are possible including those for paired and non-paired observations and when the variances are the same or different (3). To determine if the variances, V, of the two populations are the same, the variance ratio, F, is computed by the formula

$$F = \frac{s_1^2}{s_2^2} = \frac{V_1}{V_2} \qquad \text{(III-6)}$$

where $V_1 > V_2$. The calculated ratio is compared with the ratio from standard statistical tables (4). If the calculated ratio is less than the tabulated value, the variances are not statistically different and may be pooled for use in the t test by the equation

$$V = s^2 = \frac{\Sigma(x_1 - \bar{x}_1)^2 + \Sigma(x_2 - \bar{x}_2)^2}{n_1 + n_2 - 2} \qquad \text{(III-7)}$$

where $\bar{x}$ is the mean and n is the number of observations. The value of t is

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s} \left(\frac{n_1 n_2}{n_1 + n_2}\right)^{1/2} \qquad \text{(III-8)}$$

This value is compared to tabulated values for $n_1 + n_2 - 2$ degrees of freedom. Tables will give t values at various confidence levels (e.g. 90, 95, 99, 99.9%). The analyst must be cautious

in choosing the confidence level. If too high a level is selected, significant differences may not be detected. If the level selected is too low an insignificant difference may be judged significant.

Table III-2 presents the data and calculations for the comparison of two methods of analysis applied to the same sample. Six analyses were made by method 1 and seven by method 2. The averages were 11.9 and 13.1 respectively. Before computing the t value, an F ratio must be computed to test for homogeneity of variances. The calculated value 1.15 is compared with the tabular value for six degrees of freedom for the numerator and five for the denominator. The calculated value is less than 4.95, which is the tabular value at the 95% confidence level (4). The two variances are not statistically different and a variance based on both methods can be calculated. The variance based on both methods is 0.870; the standard deviation is 0.9333. The calculated value of t, disregarding the sign, is 2.31 which should be compared to the tabular values of 2.201 for 95% and 3.106 for 99% confidence levels (4).

Since the calculated value of t is greater than 2.201, in at least 95 cases out of 100 such a t value indicates a true difference between the two methods while 5 times out of 100 this value could have occured by chance alone. Since the calculated t value is less than 3.106 it can not be stated with 99% certainty that the methods give different results. A result which is positive at the 95% level is regarded as significant while a positive result at the 99% level is highly significant. In this case, it appears that the two methods give different results, but to decide with greater certainty, more tests should be run.

Table III-2. COMPARISON OF TWO METHODS OF ANALYSIS BY STATISTICAL TESTING

Method 1: 11.3, 12.2, 11.5, 13.0, 10.5, 12.4
Method 2: 13.5, 13.0, 14.0, 12.1, 11.9, 14.5, 12.7
Averages and Variances:

$\bar{x}_1 = 11.9$ $\quad v_1 = 0.806$

$\bar{x}_2 = 13.1$ $\quad v_2 = 0.923$

F test:

$$F = \frac{0.923}{0.806} = 1.15$$

Variance based on both methods:

$$v = \frac{4.03 + 5.54}{11} = 0.870$$

$$s = (0.87)^{1/2} = 0.933$$

t test:

$$t = \frac{11.9 - 13.1}{0.933} \left(\frac{6 \times 7}{13}\right)^{1/2} = -2.31$$

B. Sampling Programs

The goals of any study must be established before a valid program of sampling, analysis and interpretation can begin. A satisfactory sampling program for a water pollution study can then be designed with the assistance of scientists from all disciplines involved. Preliminary information including the number of outfalls, their locations, and the types and quantities of wastes being discharged will greatly simplify the process of designing a sampling program.

No general procedures for the establishment of a satisfactory sampling program applicable to all situations can be stated. The composition of wastewater or natural water is dependent upon many factors as indicated in the previous chapter. To satisfy the re-

quirements of many studies, few samples will be required. This is often the case in surveys of industrial effluents. For other studies frequent sampling at many locations may be required.

In any study, certain basic criteria are required in the sampling program. To describe the environment by the use of such statistics as a mean and variance of a finite number of samples, a valid sampling program must be adopted. Samples should be randomly collected to permit statistical evaluation. In practice, random sampling is infrequently used; it is common practice to sample at regular intervals. This always leads to the possibility that the results will be biased because of a cyclic fluctuation in concentration which is in phase with the sampling program. Such bias will not occur if the samples are collected with a frequency greater than the cyclic variation of the environment. Dissolved oxygen, for examply, undergoes a diurnal variation. Photosynthesis of phytoplankton during daytime may result in supersaturation of oxygen in the surface water of lakes, while at night respiration may result in undersaturation of oxygen. It is possible to describe this diurnal variation by collecting oxygen samples at regular intervals which are short in comparison to its cyclic variation. If, however, samples are collected daily, the data may be incorrectly interpreted.

The number of samples required to describe a natural water depends on the variability of the constituent to be analyzed. The sampling program should be flexible enough to permit changes if it seems desireable. The total number of samples from all locations which can be collected is governed by the facilities of the analytical laboratory. Too frequently the samples are divided among too many stations. The collection of a larger number of samples at fewer stations permits statistical analysis of the data with much more reliability of the results.

Factors which should be considered in the selection of sampling sites have been discussed by Velz (9). During periods of relatively steady flow data the data will be much easier to interpret than during periods of highly varying flow. In general, sampling of streams should be conducted downstream from outfalls and tributaries at a point where dispersion throughout the stream

is complete. Sampling too close to these discharges may result in erratic results. If sampling cannot be conducted at a point where complete mixing takes place, samples should be taken from the stream above its mouth. Physical characteristics of some rivers may require the collection of samples at many points across the channel and at different depths. Analyses of streams which receive industrial waste discharges will reflect the fluctuations in these discharges. Therefore, in planning a sampling program consideration should be given to the operating schedule and waste discharge patterns of industries influencing the river. Likewise, river levels may be greatly affected by diurnal variations in the storage and discharge of water especially by hydroelectric plants.

C. Sample Collection

Most water analyses are performed on grab samples collected in plastic buckets or such samplers as Kemmerer, Van Dorn and Nansen bottles. Samplers which are programmed to collect a volume of sample at regular intervals are available. These devices generally produce a composite sample and therefore much of the data which would result from the analyses of individual samples is lost. Continuous analyses depend on the sensors being immersed in the stream or on water being pumped by the sensors. If water is pumped, the flow rate and tubing size should be chosen to minimize the time the sample is in the tubing.

The sampling procedure must be capable of providing a valid sample. Care should be exercized in the collection of samples for the analysis of dissolved gases. Usually a satisfactory sample can be obtained by slowly drawing water from the sampler into the sample bottle through a tube extending to the bottom of the bottle and allowing water to overflow until two to three times the volume of the bottle has been allowed to overflow. If samples are to be analyzed for trace metals, non-metallic samplers should be used to prevent sample contamination.

An important part of any sampling program is the provision of complete information on the source and conditions under which the samples were collected. The United States Geological Survey (7)

recommends that the following data be collected for each sample:

Surface Waters	Ground Waters
Name of water body;	Geographical and legal locations;
Location of station or site;	Depth of well;
Point of collection;	Diameter of well;
Date of collection;	Length of casing and position of screens;
Time of collection;	Method of collection;
Gauge height or water discharge;	Point of collection;
Temperature of the water;	Water bearing formation(s);
Name of collector; and	Water level;
Weather and other natural or other man-made factors that may assist in interpreting the chemical quality.	Yield of well in normal operations;
	Water temperature;
	Principal use of water;
	Name of collector;
	Data of collection;
	Appearance at time of collection; and
	Weather or other natural or man-made factors that may assist in interpreting chemical quality.

D. Sample Preservation

Analyses are of little value if the sample has undergone changes between sampling and analysis. Some analyses require lengthy procedures or specialized equipment which often cannot be adapted readily to field use. The analyst must therefore rely on samples which have been stored for some period of time. Changes in samples may be a result of physical, chemical, or biological factors, but, since all are time dependent, the shorter the storage time, the less the effect on the sample.

Some sample constituents change so rapidly that they must

be measured at the sampling site. Changes in temperature and pressure will cause the concentrations of dissolved gases (e.g., O_2, CH_4, H_2S, and CO_2) to change. It is possible to "fix" some components through appropriate chemical treatment. Sulphide may be stabilized for many hours by formation of a mixed zinc sulfide-zinc hydroxide precipitate (1). Shifts in the carbonate or sulfide equilibria through the release of gas or precipitation will cause the pH to shift and it is therefore recommended that pH measurements be made at the sampling site.

Samples for heavy metal ion analysis should be filtered at the sampling site and acidified to about pH 3.5 with glacial acetic acid (7). Acidification minimizes precipitation and adsorption onto the walls of the container. Acetic acid stimulates the growth of molds and therefore it may be necessary to add a small amount of formaldehyde to the sample as a preservative.

Strickland and Parsons (8) recommend storing samples at -40°C for nitrogen analyses but state that changes may take place even under these conditions. Samples for nitrite analysis should not be acidified since acid will act as a catalyst in the Van Slyke reaction

$$O{=}N{-}O^- + \underset{\displaystyle NH_2}{\overset{\displaystyle |}{RCHCOOH}} + H^+ \rightarrow \underset{\displaystyle OH}{\overset{\displaystyle |}{RCHCOOH}} + N_2 + H_2O$$

and low values will be obtained. Mercuric chloride has been recommended as a preservative for inorganic nitrogen analyses (2,6).

Because of biological utilization of orthophosphate and adsorption of phosphate onto container walls, orthophosphate may be lost from solution during storage. If samples are acidified hydrolysis of polyphosphates and organic phosphates may result. Heron (5) found that in lake water with low concentrations of phosphate (less than 10 ppb PO_4-P) reduction of phosphate was due to bacterial action rather than adsorption. By treating a clean polyethylene bottle with a 5% solution of iodine in 8% potassium iodide for one week, samples could be stored for as long as two weeks without appreciable change.

E. Correllary Field Data

Concurrent with the collection of samples for subsequent chemical analysis or with continouous monitoring of chemical constituents, most programs will require other measurements to be made or samples to be collected. Many of these measurements may be made by the chemist or may be of value to him in the evaluation of chemical data. The measurements which are physical in nature are discussed in Chapter 8 and, in most laboratories, will be the responsibility of the chemist. Biological measurements of bacteria, plankton, and benthos will be useful in the assessment of pollution and close coordination of biological and chemical programs should exist for nutrient studies.

Stream flow should be measured at the time samples are collected. This information is essential to any well planned sampling program since it will determine not only the degree of dilution of wastes, but also the quantity of material contributed by run off.

REFERENCES

1) American Public Health Association, "Standard Methods for the Examination of Water and Wastewater," 12th ed., New York, N.Y., 1965, p. 293.

2) P. L. Brezonik and G. F. Lee, Air and Wat. Pollut. Int. J., 10, 549 (1966).

3) C. H. Goulden, "Methods of Statistical Analysis," 2nd ed., Chapter 4, John Wiley and Sons, New York, N.Y., 1952.

4) "Handbook of Chemistry and Physics," 49th ed., R. W. Weast, Ed., Chemical Rubber Co., Cleveland, Ohio, 1968, p. A160.

5) J. Heron, Limn. and Oceanog., 7, 316 (1962).

6) D. Jenkins, "Trace Inorganics in Water," Advances in Chemistry, No. 73, R. F. Gould, Ed., Am. Chem. Soc., Washington, D.C., 1968, p. 265.

7) F. H. Rainwater and L. L. Thatcher, "Methods for Collection and Analysis of Water Samples, U. S. Geological Survey Water-Supply Paper 1454, Washington, D.C., 1960, p. 20.

8) J. D. H. Strickland and T. R. Parsons, "A Practical Handbook of Seawater Analysis," Fisheries Research Board of Canada Bulletin 167, Ottawa, Canada, 1968, p. 82.

9) C. H. Velz, Sewage and Ind. Wastes, 22, 666 (1950).

IV. SEPARATION TECHNIQUES

A. Carbon Adsorption

The sorptive properties of activated carbon and its particular effectiveness for removing certain organic materials which impart tastes and odors to water supplies have been widely recognized. In the last five years, a specific sampling procedure using activated carbon has been recommended by the U. S. Public Health Service and currently enjoys a 'tentative method' status in Standard Methods (1). The carbon filter provides a direct means of concentrating trace organic compounds in water through passage of large volumes (up to thousands of gallons) of water through a column of 30 mesh activated carbon (Nuchar C-190, West Virginia Pulp & Paper Co., or equivalent).

After an adsorption run during which the total volume of sample flow (0.25 gpm) has been measured the carbon is removed from the column, dried and extracted with chloroform, a solvent which recovers materials most likely to be responsible for tastes and odors. Included, however, are oils, phenols, various synthetics and other materials of slight water solubility. Chloroform extraction is followed with an alcohol extraction which often removes even more organic material than was recovered with chloroform. Alcohol extracts are apparently of a different nature and usually do not have the intense odors exhibited by the chloroform solubles. Both solvent extracts are concentrated to small volumes on steam baths and then air dried overnight to reduce loss of volatile material. Final weights of the extracted materials are determined and the data recorded as:

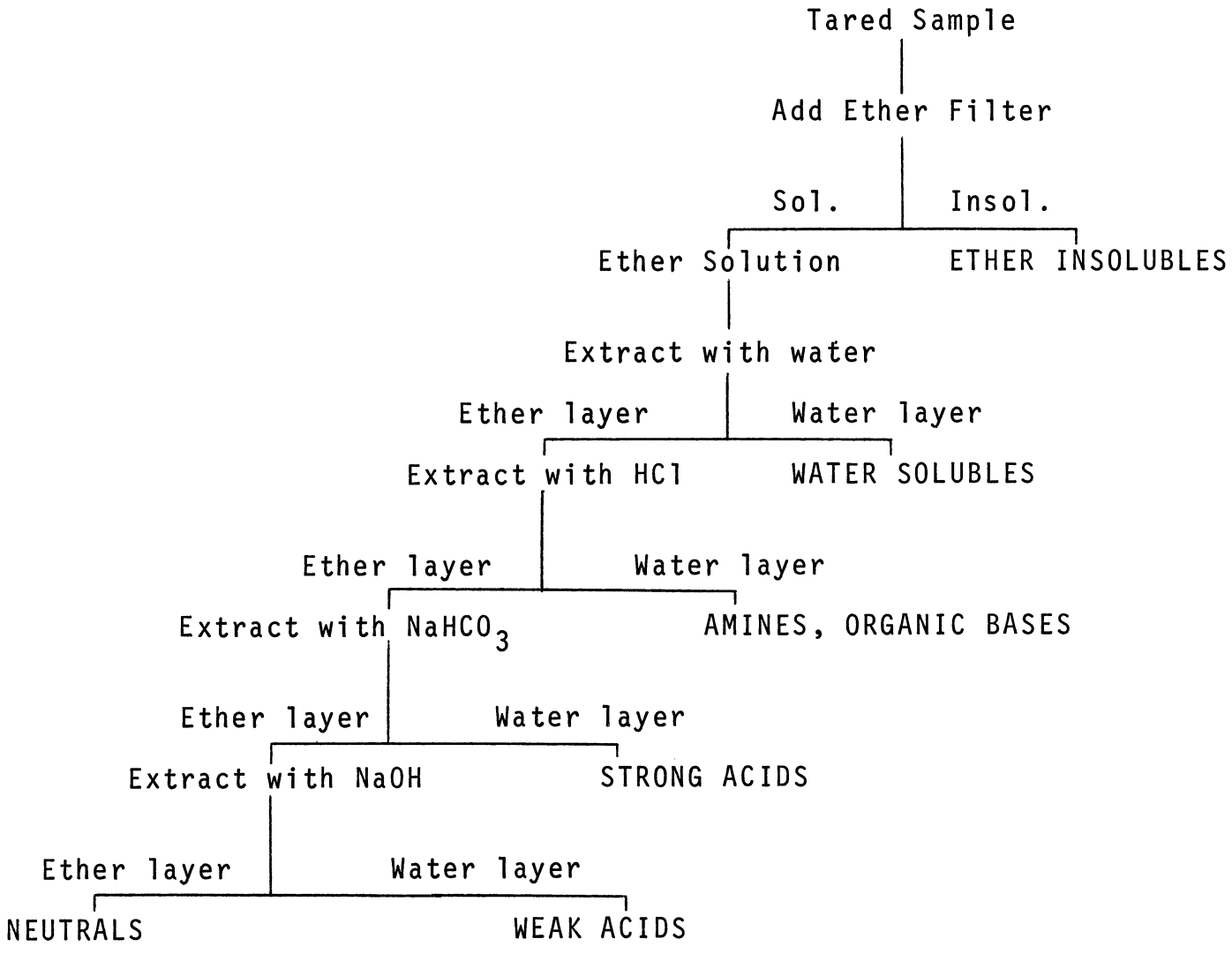
$$\underset{\mu g/l}{\text{carbon - chloroform - extract (CCE)}} = \frac{g\ CCE \times 10^6}{gal\ sample \times 3.785}$$

$$\underset{\mu g/l}{\text{carbon - alcohol - extract (CAE)}} = \frac{g\ CAE \times 10^6}{gal\ sample \times 3.785}$$

According to the U. S. Public Health Service (2) a concentration of 200 µg/l of CCE represents excessive organic contamination.

The extracts are complex mixtures and little can be determined regarding its chemical composition without further separation. Solubility fractionation as outlined in Figure IV-1 may be employed to further characterize chloroform or alcohol solubles. The Ether Insolubles are tarry or polymerized substances which do not appear important as taste or odor producers. They are removed primarily to prevent interference in later analytical steps. The Water Solubles apparently contain humic type materials of natural origin or they may be at least in part derived from sewage.

Figure IV-1. SOLUBILITY SEPARATION OF EXTRACTED ORGANIC MATERIAL



The Weak Acid fraction will contain phenols and the weaker carboxylic acids and sulfonic acids. The Strong Acids are often quite odorous (fruity or rancid); typical components being acetic, butyric and caproic acids. These substances result from biological action on sewage, industrial material or organic debris. Materials which are Neutral to the acid-base solubility fractionation can be separated on columns of silica gel by selective elution with iso-octane (aliphatic fraction), benzene (aromatic fraction) and 1:; chloroform-methanol (oxygenated fraction) and recorded as weight percentage of a given fraction. One might expect to find polynuclear hydrocarbons of the benzo-(a)-pyrene type or substances like DDT in the aromatic sub-fraction of the Neutrals solubility category.

Recoveries of organic material from the CCE and CAE procedures can be increased in some cases by removing sample turbidity with diatomite filters prior to contact with the carbon bed (3). Increased extraction yields with chloroform and alcohol are obtained if extraction of the carbon is performed at pH 3.0. Extensive research has been performed on the mechanisms of the carbon adsorption of many compounds of special interest in water supply or waste treatment (4).

B. Freeze Concentration

Concentration of water containing organic material by freezing techniques is attractive due to the structural protection offered by reduced temperatures. As solute laden aqueous samples are frozen, the ice crystals which are formed are extremely pure as solute is rejected to the liquid phase. If the process is prevented from total solidification the residual liquid will be greatly enriched in all solutes.

Freezing is accomplished by rotating a round bottom flask at a controlled rate in a temperature regulated bath (5). Baths of crushed ice and salt or ethylene glycol-dry ice are commonly used. Sample volumes of 200 ml to 20 l may be handled in batch fashion, although it is generally more convenient to freeze multiple samples of smaller volume.

Although many factors theoretically affect the efficiency of solute concentration during freezing (i.e., degree of mixing, freezing rate, nature and concentration of solutes) Shapiro (6) has contended that 99% recovery can be obtained from dilute organic solutions at volume ratios of 20:1; and since losses are non-specific overall recoveries could be determined by conductivity measurements. Other workers (7,8) notably Baker, have shown that specific organic recoveries may not be in agreement with recoveries measured by conductivity and that the process may be limited by ionic concentration in the residual liquid. Most recently, Baker (5) has studied the recoveries of several known chemical structures by freezing and observed that mixing rate is not a factor in the absence of dissolved organic salts, and further that molecular weight and size, nature and location of substituent groups do not affect recoveries in the absence of inorganic solutes. In the presence of inorganic salts, organic recoveries are markedly reduced although higher mixing rates are helpful. It is interesting and important to note that this loss of efficiency is apparently not structurally selective. Thus, as Baker has recommended, the concentration of all organic components may be adjusted according to the observed concentration efficiency of an added standard.

Some workers (9) have concentrated trace organics by a combination of vacuum distillation at temperatures not exceeding 50°C, dialysis and lyophilization (freeze drying). The lyophilizer apparatus consists of two stainless steel cylinder halves. The top half (2" x 25") has 48 attachment ports welded on to the cylinder. The bottom half (3" x 10") is a water trap designed so that the air travels down through the center to the bottom of the cylinder, then up along the outside wall to an exit port which is connected to a vacuum pump. A Dewar flask containing dry ice in acetone (-70°C) is placed around the outside of the lower cylinder to provide a coolant for the water trap. The sample is placed in a thick-walled vacuum filter flask which is then capped with a rubber stopper and joined to one of the attachment ports with vacuum tubing. All joints are sealed with a suitable high-vacuum grease. The system is then evacuated.

The overall process is relatively slow, but it leaves a dry solid residue of organic matter (high molecular weight) which is relatively ash free and can be easily re-solubilized in water.

C. Liquid-Liquid Extraction

Liquid-liquid extraction (to be referred to here as solvent extraction) has been widely used in water analysis for separating and concentrating a great variety of materials, including organic and inorganic ions, and neutral species as well. It can be performed relatively simply and inexpensively, but is also adaptable to more expensive and elaborate multi-stage and countercurrent techniques which can simultaneously increase the concentration factor and separation efficiency.

Solvent extraction avoids exposure of the extracted species to heat or solid surfaces, which may result in reactions or structure changes for labile organic materials. Unlike precipitation techniques for inorganic ions, which can result in coprecipitation of unwanted species, it can be highly selective; it can be used for very small quantities of material.

C.1. Principles

In order to perform a solvent extraction on an aqueous species, it is necessary for the extracting solvent to be essentially immiscible in the water, and vice versa. In practice there is always some slight miscibility on both parts. The extracting solvent is shaken with the aqueous solution for a time sufficient for the extractable solute to equilibrate between the two phases; at this time, the phases are permitted to separate and the solution of the extracting solvent containing the extracted solute is removed from contact with the water and utilized as required, either for further separation and concentration, or directly in analysis. The smaller the volume of the extracting solvent utilized in this process, the greater will be the concentration factor, but the smaller will be the recovery; the reverse also holds true.

The distribution equilibrium between a solute that is non-ionic and is in the same molecular form in the two phases (i.e., water and extracting organic solvent) is essentially equal to the ratio of its solubilities in the two phases. This holds either when the solutions are ideal, or are dilute enough to behave in an ideal fashion. For such a non-ionic solute A distributed between water, designated by "W", and an organic solvent, designated by "O", the equilibrium ratios of concentrations may be expressed as

$$P = [A]_O/[A]_W \qquad \text{(IV-1)}$$

which is the Nernst partition law; P is defined as the partition coefficient (15). For many species, particularly those which are charged, can dissociate, or are in different forms of aggregation in the two liquid phases, the partition coefficient can vary considerably with concentration, changes in pH, and the addition of salt or complexing agents.

The fraction of material originally present in the water phase extracted by the organic solvent may be derived from Equation IV-1 to give

$$F_E = 1/[1 + V_W/(V_O P)] \qquad \text{(IV-2)}$$

with F_E as the fraction extracted and V_W and V_O are the volumes of the water and extracting organic solvent, respectively. Thus, the greater the ratio V_O/V_W and the greater the value of P, the greater will be the fraction of material extracted from the water into the organic solvent phase, approaching unity in the limit. In order to increase the recoverability of a species in solvent extraction, it may be necessary to perform a series of extractions on the water, each time using a fresh solvent. With constant values of P and using the same volume of organic solvent in each of n successive extractions, the total fraction extracted is then

$$F_E \text{ (multiple)} = 1 - (1 - F_E)^n \qquad \text{(IV-3}$$

Thus, for example, if $F_E = 0.9$ for one extraction, for two successive

extractions F_E = 0.99. Both multi-stage (10) and continuous countercurrent extractors (14) have been developed which make use of this increased recovery with exposure to fresh solvent.

Another important consideration is the concentration factor, the ratio between the concentration of extracted material in the organic phase at equilibrium, compared to that initially present in the water solution. Using Equation IV-1 this may be shown to be

$$\text{Concentration factor} = 1/(1/P + V_O/V_W) \qquad \text{(IV-4)}$$

Thus, the concentration factor will increase with the partition coefficient, but decrease with increasing V_O/V_W.

In extracting inorganics, such as metal ions, from water, a common technique is to use an organic complex or chelating agent which greatly increases the solubility of the metal in the organic solvent, thereby increasing its partition coefficient (15). In such an extraction, both the uncharged metal-chelate molecule and the organic chelating agent itself have separate partition equilibria. Because these chelates are generally weak acids or bases, pH will have a great effect on their ability to bind the ion, as well as on their own partition coefficient. The combination of these effects is such as to cause pH to have a high degree of control in the extraction of metals by organic solvents using chelating agents. This can be very useful in selectively extracting certain metals, but not others in a mixture.

C.2. Applications

In one recent application solvent extraction was used to concentrate chlorinated hydrocarbon pesticides from water using a semi-automatic device (13). Following extraction of 850 ml of water by 50 ml of various solvents, the latter solutions were then evaporated to 0.5 ml prior to gas chromatographic analysis. Compared to a manual extraction process this semi-automatic technique was about 50% more efficient, recoveries varying from 69 to 95% in the combined steps of extraction and evaporation.

In an investigation on taste and odor producing organics in river and municipal water, an 18 stage continuous countercurrent

extractor was used to concentrate prior to analysis (12). Several solvents were tested, and it was concluded that methyl isobutyl ketone was the best extractant for phenol, and generally good for other organics. Using an aqueous feed of about 0.1 mg/l of phenol, recovery was 94%. Extractions of mixtures containing O-cresol, guaiacol and phenol led to recoveries of 88 to 99%, depending on the solution-solvent ratio and agitator speed. In using this technique to extract river water under the same conditions used for municipal water, the sample-solvent mixture tended to emulsify, and it was necessary to reduce the agitator speed. In one such extraction of river water containing 0.07 mg/l of phenol, the recovery efficiency of the latter was 52%.

Many analyses of metals involve their chelation, followed by solvent extraction. One recent study was made of a comparison of the extraction from sea water of iron (II) complexes with orthophenanthroline, bathophenanthroline, and 2,4,6-tripyridyl-symtriazine (TPTZ), the extracting solvent being propylene carbonate (17). It was found that, using these chelates, iron (II) was readily extracted from sea water at low concentrations and could then be analyzed in the propylene carbonate spectrophotometrically. For iron (II) in the concentration range of 5 to 27 µg/l, the average error was 5%. Depending on the chelate used, the pH range of extraction was from 2 to 9.

Solvent extraction of metals is frequently used prior to atomic absorption analysis, not only to concentrate, but also because of the increased sensitivity of the method with organic solvents. A common solvent for this purpose is methyl isobutyl ketone (MIBK). One study using this solvent involved the extraction of cobalt, nickel and lead in fresh water, using ammonium pyrrolidine diothiocarbomate (APDC) as the chelating agent (11). In these studies the water-MIBK ratio was 20/1 and the pH in the water adjusted to 2.8 prior to extraction. This pH value was critical for lead, but could be as high as 5 for cobalt and nickel. It was concluded that this extraction technique in combination with atomic absorption spectrophotometry offered a rapid, simple, accurate, and sensitive method for analyzing these metals in fresh waters. A similar method was studied for iron, copper, zinc,

lead and cadmium, using diethyldithiocarbomate as the chelating agent (16). As a result of the metals being concentrated in the extraction process, as well as due to the increased sensitivity of the atomic absorption analysis in the MIBK, the detection limit was lowered by a factor of 15 to 30 for each metal compared to its direct analysis in water.

These few examples demonstrate part of the range of applicability of solvent extraction as a tool to facilitate water analysis. It is a widely used technique, both for concentrating and separating a great variety of micro and macro species in water.

D. Ion Exchange[1]

Ion exchange as a concentration and separation technique has been in use for some 50 years. One early method by Bahrdt in 1927 used a sodium zeolite column to remove calcium and magnesium from a natural water because of their interference in a sulfate analysis (18). The use of synthetic zeolites in ion exchange is limited, however, because of their narrow useful range of pH and the difficulty in achieving quantitative elution. In the 1930's, organic cation and anion exchange resins were synthesized and analytical applications developed, principally by Samuelson (19). The theory of ion exchange equilibria, kinetics and chromatography has been treated by Helfferich (20), and Samuelson (18) and Inczedy (21) have comprehensively considered their analytical applications.

Ion exchange in water analysis may be used for determining the total equivalents of salt present, to concentrate ions, and to separate them from non-electrolytes, as well as from other ions of similar or opposite charge. It is applicable to organic and inorganic ions, and is particularly useful in removing interferences so as to facilitate subsequent analysis. Ion exchange is a fast

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1. Portions of this discussion are taken, with the kind permission of the publisher, from the article by J. B. Andelman and S. C. Caruso, "Concentration and Separation Techniques" in "Handbook of Water and Water Pollution," L. Ciaccio, ed., Marcel Dekker, Inc., New York. In preparation.

and simple technique, which usually yields high accuracy and recovery and requires relatively little judgement, thus making it readily adaptable for routine analyses.

D.1. Ion exchange equilibria and kinetics

When an ion exchanger is equilibrated with an ambient solution containing two exchangeable ions, univalent cations for example, the exchange process is stoichiometric and the equilibrium reaction is

$$A^+ + B_R^+ \rightleftarrows A_R^+ + B^+ \qquad \text{(IV-5)}$$

with the subscript R referring to species in the resin phase. (The term "resin" will be used for convenience to designate the ion exchange material, since synthetic resins are the principal ion exchange material in current use.) The absence of this subscript refers to species in the ambient solution phase. For this reaction an equilibrium expression may be written

$$K_B^A = \frac{(A^+)_R \times (B^+)}{(A^+) \times (B^+)_R} \qquad \text{(IV-6)}$$

with K_B^A being the equilibrium constant, which is generally referred to as the selectivity coefficient. The terms in parentheses refer to concentrations. K_B^A is a simple measure of the ability of the resin to select A^+ over B^+. For example, if in the ambient solution at equilibrium $(A^+) = (B^+)$, then $K_B^A = (A^+)_R/(B^+)_R$. The larger the selectivity coefficient, the greater is the efficiency of separating the ions of like charge by ion exchange.

Selectivity scales for various ions and resin types have been constructed. They indicate the relative affinities of a given resin for various ions. For example, with a typical strong acid resin an affinity series for univalent cations is (18)

$$Ag > Cs > Rb > K > NH_4 > Na > H > Li.$$

A similar scale for divalent ions with the same type of resin is

Ba > Pb > Sr > Ca > Ni > Cd > Cu > Au > Mg.

The selectivity coefficient for a given pair of exchanging ions is affected by several factors. One of the most important is the basic chemical structure of the resin. When, for example, the cation exchanging sites are of the strong acid type, such as sulfonate, the resin affinity for hydrogen ion is generally low. In contrast, a weak acid cation exchange resin, those with carboxyl sites, have a high affinity for hydrogen ion. Other factors that affect the selectivity coefficient are composition of the exchange ions in the resin phase, tightness of the resin structure, temperature, and ambient solution concentration of exchange ions and other solutes.

Most of the ion exchange sites in a typical resin are located within the matrix or pore structure. Thus, for a typical ion exchange process to occur, such as represented by Equation IV-5, the ions must pass through the resin matrix and across a liquid film boundary layer at the resin solution interface. The rate determining step in the exchange process could then be (22)

1) diffusion in the boundary layer (film diffusion)
2) diffusion in the resin phase (particle diffusion)
or 3) chemical exchange at the exchange sites.

In most cases the chemical exchange is sufficiently rapid so as not to be rate limiting. In one study of alkali metal ion exchange it was found that at ambient solution concentrations below 0.003M the exchange kinetics could be considered to be film diffusion limited; above 0.1M the process was particle diffusion limited.

D.2. Column operation

The rate of the exchange process and the selectivity coefficient are the principal factors that affect column operations. The latter are more widely used than batch processes because they lend themselves more readily to continuous operation, the exchange reaction

approaches completion because it is continuously displaced, and they can be used in chromatographic separations.

If the purpose of ion exchange primarily is to concentrate either a single ion or a mixture of similarly charged ions, the solution may be passed through the column, the resin behind the advancing front being left with, for example, the cation to be concentrated, A^+, or a mixture of such ions A_1^+, A_2^+, A^+_3, etc. At this point the column may be washed with distilled water, the front remaining fixed in place. Next the column is eluted with an electrolyte, perhaps containing C^+, and the adsorbed A^+ ions move down the column ahead of the newly advancing C^+-A^+ front. If the concentration of the eluant C^+ solution is significantly larger than the original A^+ solution, then the latter in the effluent will appear more concentrated than originally. This procedure also serves to remove either anions or neutral species originally present in the A^+ solution, since when A^+ is initially adsorbed by the resin, they continue through the column with B^+ and appear with it in the effluent; any remaining quantities of anions or neutral species are removed generally in the distilled water wash prior to elution.

When ion exchange is being used to separate ions of like charge sign, a useful technique is to adsorb the mixture, but utilize only a small portion of the top of the column. This is generally followed by washing the column to remove any excess co-ions and neutral species, and finally eluting by either the technique of selective displacement with various eluants, or elution chromatography.

In elution chromatography, the mixture of similarly charged ions at the top of the column is eluted by one eluant which displaces all of them, but at different rates depending on their relative selectivities. As the eluant moves down the column, the bands of the various ions being eluted move with it, the peaks broadening as they move. The positions of the bands of such a mixture of three cations, A_1^+, A_2^+, and A_3^+ at two different times in the elution process are shown in Figure IV-2B. In this case A_1^+ and A_2^+ are not completely separated. Thus, although A_3^+ may be completely collected

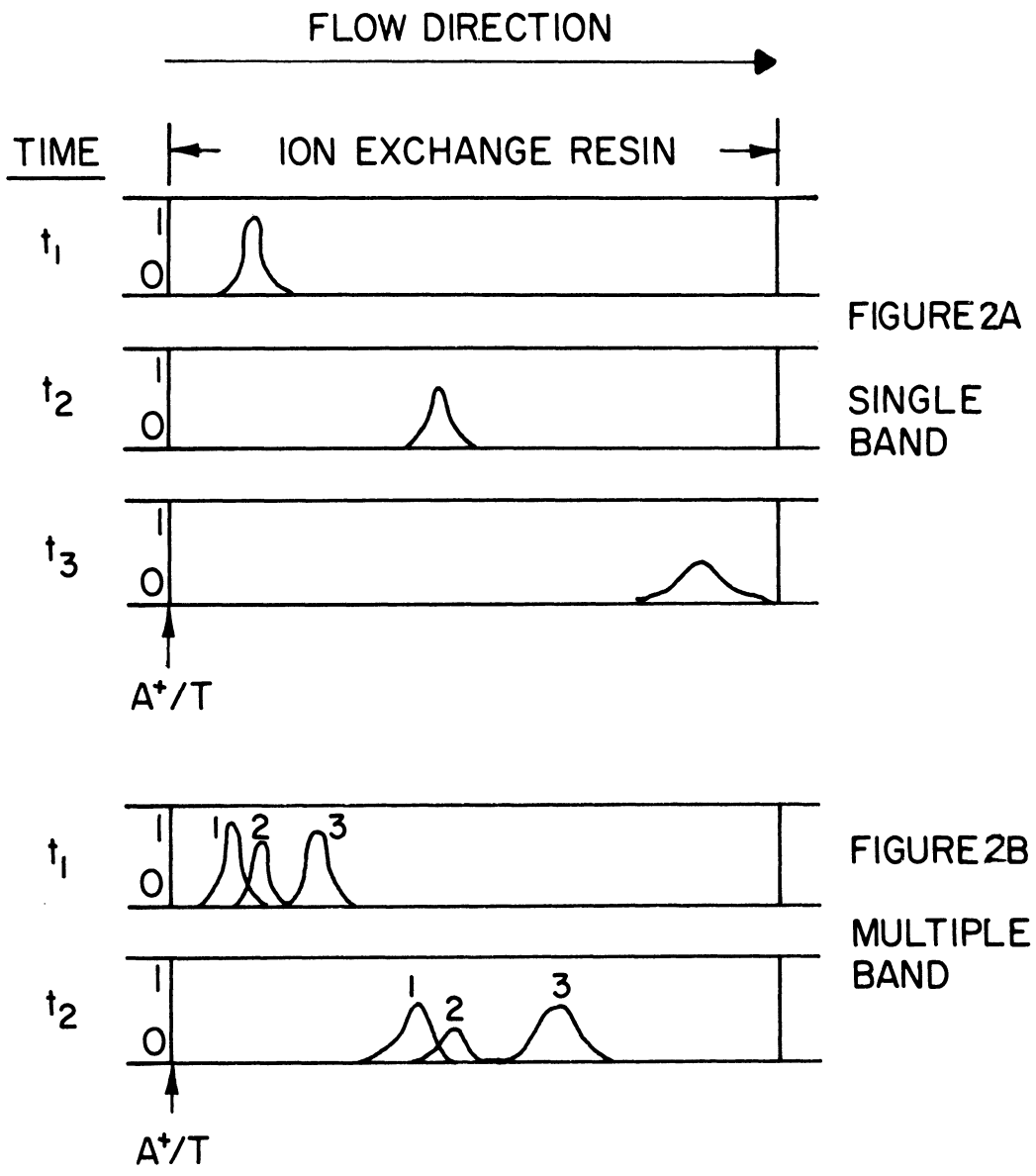


FIGURE IV-2. ION EXCHANGE ELUTION PROCESS

in one or more fractions not containing the other A^+ ions, A_1^+ and A_2^+ cannot. The similar movement of a single eluted substance is shown in Figure IV-2A.

D.3. Applications

There have been numerous reported applications of ion exchange in water analysis, only a few of which will be briefly discussed in order to indicate their scope. The total salt concentration in natural and boiler waters has been determined by adsorbing the latter onto cation exchange resins in the hydrogen form and titrating the displaced hydrogen ions. In one such technique a batch equilibrium method was used, corrections being made for alkalinity, which was determined separately, and the expected average deviation was 0.12 milliequivalents per liter of total cations; it was noted that, for natural waters with low potassium and sodium content, the total cation content is a good estimate of sodium (23).

A scheme of analysis for industrial waters has been presented using strong acid and strong base resins in order to determine calcium, magnesium, copper, iron (III), chromium (III), chloride, sulfate, metaphosphate, orthophosphate, silicate and chromate(24). The method was developed so as to remove chromate interferences in the colorimetric determinations of orthophosphate, silicate and metaphosphate, and in the chelometric analysis of calcium and magnesium; it also removed copper and iron (III) which interfered in the latter analysis. In the analysis of the anions hydroxylamine hydrochloride is added to the test solution to reduce the chromate ion to chromium (III), which is then removed in subsequent passage through the cation exchange resin. The anions in the effluent are then analyzed colorimetrically. Similarly chromium (III) in the test solution is oxidized with peroxide to chromate and separated from the cations by adsorption on the anion exchange resin. Copper and iron (III) are then determined directly in the effluent. For the calcium and magnesium analyses, the copper and iron (III) are then complexed with cyanide to form $Cu(CN)_4^{-2}$ and $Fe(CN)_6^{-3}$ which are removed in passage over an anion exchange resin, the effluent then being analysed by EDTA titrations. The complete scheme of

of analysis generally gave results which agreed well with conventional methods of analysis of cooling water samples.

Using a strong acid and a weak base resin column in series, a field procedure was developed to enrich and analyze natural waters (25). Following uptake on the columns, the latter were eluted by hydrochloric acid and ammonia, respectively. It was found that uptake and recovery was complete for sodium, potassium, magnesium, calcium, manganese (II), chloride, and sulfate. Variable amounts of phosphate and iron (III) were adsorbed onto the resin, the remainder passing through as non-exchangeable complexes or associated with humus.

A scheme for the analysis of the major cations in sea water has been developed, using a resin column to adsorb the cations and then successively eluting with a sequence of different eluants (26). After adsorbing 30 ml of sea water on the resin, potassium and sodium were eluted with 0.15M ammonium chloride; then calcium with a solution of 0.35M ammonium chloride; next magnesium with 1M ammonium acetylacetonate at pH 9.6; and finally strontium with 2M nitric acid. A variety of analytical methods were used for the different fractions.

Several applications of ion exchange primarily for the purpose of concentrating ions have been reported. A chelating resin has been used with industrial waste waters in order to concentrate multivalent cations by a factor of 10 to 20 prior to analysis by atomic absorption spectrophotometry (27). It was noted that the metals were held more strongly by the chelating resin than by a typical sulfonic acid resin. In this technique the water samples were buffered to a pH of 5.5, sorbed onto the resin, and then eluted with 8M nitric acid. The sensitivity of the method was 5 ppb for copper, cadmium and zinc, and 50 ppb for lead (II), nickel (II) and iron (III).

One of the most prevalent uses of ion exchange in water analysis is the removal of interfering species. One such method for fluoride involved the use of an anion exchange resin (28). The test solution is passed through the resin column in the acetate state, the fluoride being retained, and potentially interfering cations appearing in the effluent. The fluoride is then eluted from the column with 0.005M beryllium (II) in 0.1M acetic acid, the eluted species

presumably being BeF_4^{-2}, and the SPADNS method used to analyze the fluoride. If aluminum is present in the test solution it must be first chelated prior to the ion exchange step. Using synthetic fluoride solutions of 0.5 and 1.0 mg/l, the accuracy and precision of the method were each with approximately 10 percent, even with the following individual or mixtures of added possible interferences: 200 mg/l orthophosphate, 400 mg/l calcium carbonate, 1000 mg/l chloride, 2 mg/l hexametaphosphate, 1000 mg/l sulfate, 0.5 mg/l chlorine, and 5 mg/l aluminum. As with the previous cation exchange method, this technique eliminated the need for distillation.

Ion exchange is also a useful tool in the analysis of organic constituents in natural waters. An example of such an application is the analysis of paraquat, which is the common name for the cation 1,1-dimethyl-4,4-bipyridilium, used as a herbicide for weed control (29). Plant constituents and other organics in water may interfere with the spectrophotometric analysis and are removed by this ion exchange technique. After passing the aqueous test solution through the cation exchange resin column, the latter is washed with 2N HCl, then 2.5% NH_4Cl. The paraquat is then eluted with saturated NH_4Cl a and analyzed spectrophotometrically. The selection of the type of resin was critical, the criteria being that the paraquat, but not the interfering species adsorb well onto the column, that much of the light-absorbing material retained by the resin be eluted prior to the paraquat, and that the latter be eluted with high efficiency. The procedure was found useful for waters containing substances absorbing light in the region of 256 mμ, the absorption maximum for unreduced paraquat. For water samples of 50 to 500 ml the expected recovery of the method is 85 to 100%.

In concluding this discussion of ion exchange in water analysis, it is of interest to note an application for the removal of interferences in the low level measurement of oxygen in boiler waters (30). Such waters frequently contain iron (II) and hydrazine, the latter being added as a scavenger for dissolved oxygen. In the Winkler analysis of these waters containing oxygen in the range of 0.01 to 0.04 mg/l, hydrazine and iron (II) were found to interfere when in the range of 0.04 to 0.2 mg/l and 0.1 to 1.2 mg/l respectively. By first passing the test solution through a cation exchange resin these interferences were successfully removed.

E. Chromatography

In many cases the most difficult part of an organic analysis is the separation of mixed components into relatively pure fractions prior to subsequent analytical operations. Within the last fifteen years several separation techniques have proven so successful that they serve today not only as separation tools but as sensitive methods of analysis per se. The various separation or "chromatographic" techniques are categorized primarily on an operational rather than a conceptual basis. Thus, the terms, paper, column, thin layer, gas-liquid, and ion exchange chromatography, for example, refer to difficult procedural applications of the same fundamental concept.

E.1. General Principles

A rigorous presentation of chromatographic theory is beyond the scope of this manual. Adequate treatments of theory are available in the literature (31-34) although such presentations are often confined to a specific chromatographic technique.

All forms of chromatography consist of at least two immiscible phases, one of which is static and the other is mobile. The static phase may be a solid, or a liquid held on a solid, whereas the mobile phase may be a gas, a liquid or a dissolved solid. In all cases the mobile phase either is or contains the sample. Types of chromatography may be classified according to the nature of these phases in any particular combination as shown in Table E-1.

Separation of components is due to phase equilibria that occur between the sample components and the static mobile phases. This results in a distribution or "partitioning" of the sample between the two phases. At equilibrium a solute will distribute itself between two immiscible phases so that its chemical potential (μ) or escaping tendency is equal. Therefore,

$$\mu_1 = \mu_1^* + RT \ln C_1 \qquad \text{(static phase)}$$

$$\mu_2 = \mu_2^* + RT \ln C_2 \qquad \text{(mobile phase)}$$

Table E-1. Classification of Chromatographic Methods

Moving Phase	Static Phase	Name of Method
L*	S	column chromatography thin layer chromatography ion exchange chromatography≠
L	L	column chromatography paper chromatography
G	S	gas-solid chromatography molecular sieves
G	L	gas-liquid chromatography

* L = Liquid; G = Gas; S = Solid

≠ Mobile phase is dissolved solid

and at equilibrium

$$\mu_1 = \mu_2$$

$$\ln \frac{C_1}{C_2} = \frac{\mu_1 - \mu_2^*}{RT}$$

$$\frac{C_1}{C_2} = \exp\left(\frac{\mu_1^* - \mu_2^*}{RT}\right) = K$$

The exponential term is independent of concentration and is known as the "partition coefficient" (K). Each particular solute-static phase-mobile phase combination will have a characteristic coefficient that will determine the migration rate of each solute through the system at any given temperature and flow rate of mobile phase. Regardless of the nature of the force responsible for partitioning (i.e., solubility, adsorption, chemical bonding) the intensity of the force will vary among the components of a sample. Therefore, as contact between the phases increases the separation of the components will increase.

E.2. Gas-Liquid Chromatography

In this form of chromatography volatile materials are separated by passing a gas stream over a finely divided solid static phase which may be coated with a high boiling liquid. Many variations in apparati are (commercially) available in varying degrees of sophistication and cost ($1000 - $15,000). A basic block diagram of a typical instrument is shown in Figure IV-3. A "chromatogram" is obtained as a record on a strip chart recorder which continuously receives a signal from a detector monitoring some physical or chemical property of the effluent stream. Any material having an appreciable vapor pressure (1-1000 mm) at the temperature of operation (0-400^{o}C) can be satisfactorily eluted.

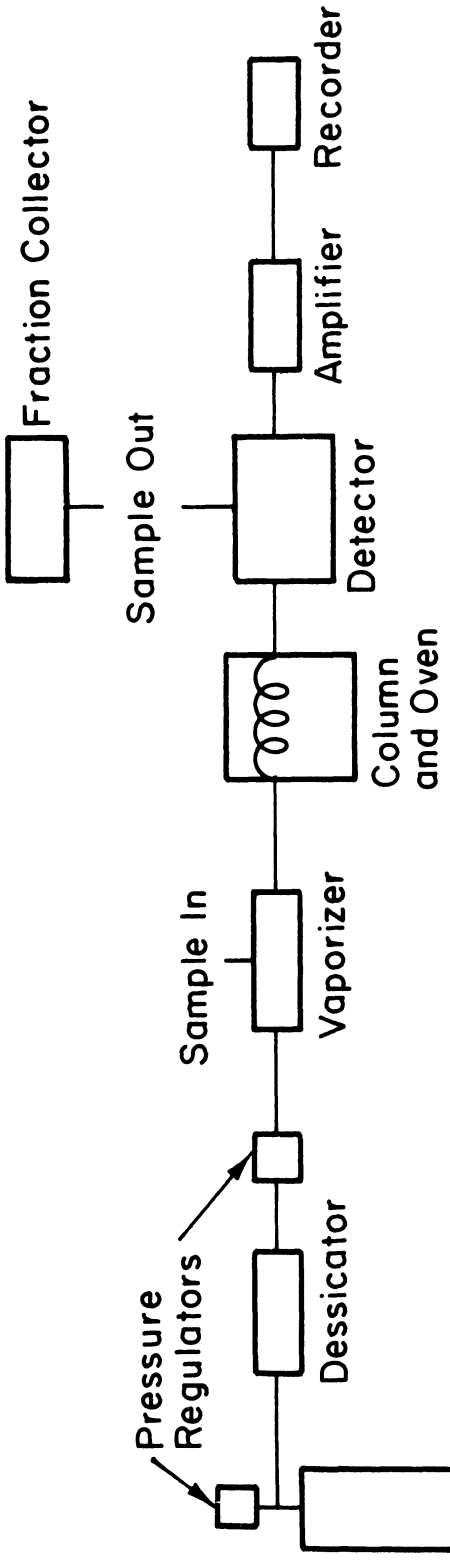


FIGURE IV-3. BLOCK DIAGRAM OF TYPICAL GAS CHROMATOGRAPH

E.2.a. Separation Process

The partitioning of sample components in the column is subject to plate theory analysis (32). Employing this theory as a model it is possible to identify operational characteristics required for ideal chromatographic separation. Gas flow through the column must be constant and no axial diffusion permitted in any phase; i.e., components must enter and leave the two phases simultaneously, thus providing instantaneous equilibrium. For any column of given composition and geometry an optimum gas flow will exist for ideal separation of two sample components. At flows less than optimum, longitudinal diffusion occurs and column efficiency is reduced. For ordinary columns (5-6 mm I.D.) 20 ml/min is sufficient to avoid this problem. At high flows insufficient time is allowed for equilibration. Column efficiency is related to the number of theoretical plates calculable from plate theory (31), and is largest when the ratio of the volume of carrier flow needed for elution of a component to the width of the peak is large.

E.2.b. Columns

Chromatographic columns are generally of three types:

(i) analytical: liquid coated or solid support, usually restricted to 20 ft. lengths due to pressure drop; 1/4" to 1/8" O.D., 0.05 - 0.01" I.D.

(ii) capillary: liquid coated on inner wall of tubing; 100-200 ft.; 1/16" O.D., 0.01" I.D.

(iii) preparative: about 20 ft. maximum length; usually 3/8" O.D.

All columns are constructed of stainless steel, glass or aluminum with stainless steel being most popular because of its cost and durability. They are often shaped in coils because of their great lengths and in such cases the coil diameter should be at least ten times the column diameter to avoid diffusion effects.

Many columns are packed with solids used primarily as support for active liquid coatings. Solid supports should be inert, have large surface areas and be of uniform size. Basic support materials are:

(i) Chromosorb P: crushed firebrick; shows some adsorption effects; used for high efficiency packed columns. Surface area about 4 m^2/g.

(ii) Chromosorb W: prepared from filter aids; inert; less efficient than Chromosorb P. Surface area about 1 m^2/g.

Liquid phases used to coat solid supports are usually high boiling polymers, such as ethylene oxide polymers, high molecular weight alcohols, oils and greases. Proper selection of the liquid phase is essential to successful chromatography and references are available (35) which describe the types of liquid coatings needed for a variety of specific applications. Liquid phases are coated on solids in the 2-10 wt% range; lower loadings require very inert solid support and higher loadings give reduced efficiency. Vapor pressures of liquids coatings must be low (<0.01 mm) at operating temperatures to prevent "bleeding" during operation. Bleeding not only shortens column life but reduces efficiency and interferes with detection. Each liquid coating has therefore a maximum recommended temperature (MRT) for operation.

Columns may be obtained commercially and assembled to specification, however, this procedure is often expensive. Stock quantities of solid support and pure liquid phases in Kg quantities may be purchased at reasonable prices and the coating performed in the laboratory. The liquid phase is dissolved in an appropriate solvent and mixed with the solid support in either a rotary evaporator or a saucepan with shaking. New columns must be conditioned by running overnight at $20^{o}C$ above normal operating temperature with small carrier gas flow (5-10 ml/min).

Gas flow rates through columns during operation varies widely but is generally in the 20 to 60 ml/min range for 1/8" columns and in the 80 to 200 ml/min range for 1/4" columns.

E.2.c. Sample Introduction

Liquid and gas samples may be injected with a calibrated syringe through a septum onto the head end of the column. Injector blocks on most instruments are maintained 8-$10^{o}C$ warmer than the oven to flash evaporate liquid samples and prevent condensation. Sample volumes

must be as small as possible and injection performed as swiftly as possible to avoid non-ideal effects. Since the injector block is generally at 5 to perhaps 60 psi pressure extreme care must be given to injection technique or non-reproducible data will result.

E.2.d. Carrier Gas

The nature of the inert gas used to carry the sample through the column depends primarily on the analysis and the type of detector. Helium, Argon, Hydrogen and Nitrogen are frequently used, although any gas that is distinguishable in the detector from sample components may be used. The use of impure carrier gas may cause extraneous peaks on the chromatogram or baseline drift of the recorder.

Commercial grade gases may be dried by passing through a molecular sieve trap which can be reconditioned by heating to 400^{o}C for four hours with a gas stream passing through it. A convenient check on the impurities in a carrier gas supply can be performed by withdrawing a syringe load of carrier and re-injecting it at operating conditions. Impurities will then enter the column as a plug flow and appear in the detector in addition to background impurities.

E.2.e. Detectors

Ideally, detectors give one signal when carrier gas is present and a different signal when carrier gas plus a sample component is present. (The signal produced by the carrier gas alone is adjusted to the recorder baseline or zero.)

Detectors vary widely in the mechanism of their response and in their sensitivities and specificities. It is generally true that as the sensitivity of detectors increases the range of compounds they are capable of responding to decreases. Thus the flame ionization detector is much more sensitive than the thermal conductivity detector, but the former responds to only organic molecules whereas the latter responds to any molecule different from the carrier gas.

Detectors are often characterized by the minimum detectable quantity that results in signal production (MDQ); the concentration range over which the detector responds (Dynamic Range, DR); the concentration range over which the detector response is linear (LDR).

(1) Thermal Conductivity Detection

A heated platinum filament will lose heat mainly but conduction through surrounding gas. The heat conductivity of the gas depends on the mobility of the gas molecules which is a function of molecular weight. Thus if the composition of a gas stream passing over heated Pt filaments changes (due to elution of sample component) the filament temperature will change. The filaments in commercial chromatographs are made part of a Wheatstone Bridge so that resistance changes due to the temperature effects can be measured, amplified and recorded. Therman conductivity (TC) filaments are usually coiled and possess a high temperature coefficient of resistance. The wires are approximately $100^{o}C$ warmer than surrounding parts of the detector which are at approximately $300^{o}C$.

MDQ	2-5 micrograms
Response	all components except carrier
LDR	10,000
Carrier Gas	He
Temp. Limit	450^{o}

(2) Flame Ionization Detection

Carrier gas and sample mixtures leaving the column are burned in an H_2-O_2 flame at a quartz tipped jet.

$$H_2 + O_2 + \text{Organic} \rightarrow CO_2 + H_2O + e^- + \text{ions}$$

$$\Sigma\, e^- + \text{ions} \rightarrow \text{current}$$

An ion eollector electrode is situated directly above the flame and is maintained at a potential of 200-300 volts. Current flows from the collector electrode to an electrometer.

MDQ	10^{-11}g
Response	All organic compounds. Insensitive to all fixed gases, H_2S, CO_2, SO_2, CO, H_2O, etc.
LDR	10^6
Carrier Gas	N_2, He, Argon
Temp. Limit	$400^{o}C$

(3) Electron Capture Detection

The electron capture detector employes a tritium source (titanium tritide on steel foil) to ionize nitrogen carrier gas molecules producing slow electrons. These slow electrons migrate to the anode under a fixed voltage producing a steady durrent which is amplified by the electrometer. If a sample contains electron absorbing materials this current will be reduced. The loss of current is a measure of the amount and electron affinity of the component.

$$\beta + N_2 \rightarrow N_2^+ + e^-_{slow}$$

$$e^-_{slow} + X \rightarrow X^-$$

Loss of e^- → Reduces current

MDQ	MDQ	Variable, sensitive to halides, metal-organics, s-compounds
	LDR	500
	Carrier Gas	N_2 (very pure)
	Temp. Limit	220°C

(4) Microcoulometric Detection

This process detects components that will produce unionized compounds with Ag^+, e.g., sulfur and the halogens. The detector consists of an electrolytic cell containing silver electrodes immersed in silver acetate. When a component which reacts with Ag^+ by dissolution of the Ag electrode. The current flow is amplified and recorded.

E.2.f. Data Interpretation

Information obtained directly from the chromatogram is of both qualitative and quantitative significance. Frequently used parameters are:

i) Retention volume: volume of carrier gas required to elute component from injection to detection.

ii) Retention time: calculable from retention volume under conditions of constant flow; measur ble with stop watch from injection to detection.

iii) Retention distance: distance on recorder chart under constant flow and constant chart speed, from injection to detection.

iv) Adjusted Retention Volume: (Time or Distance) measured from air or solvent peak to detection of component. Eliminates column dead volume.

v) Relative Retention Volume: (Time or Distance) measured relative to standard component appearing in same chromatogram.

Relative retention data (v) are preferable as they are subject only to temperature variations in the column during development, whereas the other parameters are subject to flow variations as well. Qualitative identifications are made by comparison with known compounds on several columns. Quantitative measurements are made by correlating peak height (or area for assymetrical peaks) with concentration of standards.

Other data is often valuable for compound identification. The comparison of response ratios of a given compound analyzed by two different detectors under fixed conditions is characteristic of that compound. In addition, non-chromatographic identification of separated and collected components by derivative formation, spectrophotometric measurement, and mass spectrometry is possible.

E.3. Thin Layer Chromatography

Thin layer chromatography is analytical adsorption chromatography. It involves spreading a thin layer of adsorbent on a solid flat support such as a glass plate; applying a mixture of components to a spot on one end of the adsorbent and developing the chromatogram by immersing the tip of the coated plate in a suitable solvent. The procedure is fast and has good sensitivity for the lipophilic materials difficult to separate by paper chromatography. Excellent reviews (36) are available detailing specific adsorbent-solvent combinations for given compound types (see Chapter X).

Separated compounds may be fluorescent under UV examination of the plate or may be located with various chromogenic spray reagents. The ratio of the distance traveled by any component to that traveled by the solvent from is characteristic of a given compound. Internal standards are helpful as in gas-liquid chromatography.

REFERENCES

1) Standard Methods for the Examination of Water and Wastewater. APHA, AWWA, WPCF, 12th Edition (1965) p. 213.

2) U. S. Public Health Service Drinking Water Standards, Public Health Service Pub. 956 (1963).

3) R. T. Skrinde and H. D. Tomlinson, Jour. Water Poll. Control Federation, 35, 10, 1292 (1963).

4) Summary Report, Advanced Waste Treatment Research, AWTR-14, U. S. Department of Health, Education and Welfare, Public Health Service (1965).

5) R. A. Baker. Freeze Concentration of Microorganics in Water. Microorganic Matter in Water, ASTM STP 448, American Society for Testing and Materials, (1968) p. 65.

6) J. Shapiro. Science, 113, 3470, p. 2063 (1961).

7) S. Kobayashi and G. F. Lee. Anal. Chem., 36, 11, 2197 (1969).

8) R. A. Baker. Jour. Water Poll. Control Fed., 37, 8, 1164 (1965).

9) R. F. Christman. Chemical Structures of Color Producing Organic Substances in Water. Symposium on Organic Matter in Natural Waters, Institute of Marine Science, University of Alaska (1968).

10) L. C. Craig and O. Post, Anal. Chem., 21, 500 (1949).

11) M. J. Fishman and M. R. Midgett, "Trace Inorganics in Water", R. F. Gould, ed., Chap. 12, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

12) R. D. Hoak, Int. J. Air Water Poll., 6, 521 (1962).

13) F. K. Kawahara, J. W. Eichelberger, B. H. Reid, and H. Stierli, J. Water Poll. Control Fed., 39, 572 (1967).

14) J. J. Kolfenbach, E.R. Kooi, E. I. Fulmer, and L. A. Underkoffer, Ind. Eng. Chem., Anal. Ed., 16, 473 (1944).

15) H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, 1960.

16) J. A. Platte, "Trace Inorganics in Water," R. F. Gould, ed., Chap. 14, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

17) B. G. Stephens and H. A. Suddeth, Anal. Chem., 39, 1478 (1967)

18) O. Samuelson, Ion Exchange Separation in Analytical Chemistry, John Wiley and Sons, New York, 1963.

19) O. Samuelson, Z. Anal. Chem., 116, 329 (1939).

20) F. Helfferich, Ion Exchange, McGraw-Hill Book Co., New York, 1962.

21) J. Inczedy, Analytical Applications of Ion Exchangers, Pergamon Press, New York, 1966.

22) G. E. Boyd, A. W. Adamson, and L. S. Myers, Jr., J. Am. Chem. Soc., 69, 2836 (1947).

23) R. Navone, J. Am. Water Works Assoc., 46, 449 (1954).

24) J. W. McCoy, Anal. Chim. Acta, 6, 259 (1952).

25) F. Nydahl, Proc. Int. Assoc. Theor. Applied Limn., 11, 276 (1951).

26) R. Greenhalgh, J. P. Riley, and M. Tongudai, Anal. Chim. Acta, 36, 439 (1966).

27) D. G. Biechler, Anal. Chem.,37, 1054 (1965).

28) F. S. Kelso, J. M. Mathews, and H. P. Kramer, Anal. Chem., 36, 577 (1964).

29) A. Calderbank and S. H. Yuen, Analyst, 90, 99 (1965).

30) E. C. Potter, J. Appl. Chem., 9 645 (1959).

31) Fundamentals of Chromatography, American Association of Professors in Sanitary Engineering (AAPSE), Second Annual Workshop, University of Colorado, June (1967).

32) H. M. McNair and E. J. Boneili, Basic Gas Chromatography, Varian Aerograph, 2700 Mitchell Drive, Walnut Creek, California (1967).

33) H. G. Cassidy, Fundamentals of Chromatography, in Techniques of Organic Chemistry, Volume 10, ed. by A. Weissberger, Interscience (1957).

34) E. W. Berg, Physical and Chemical Methods of Separation, McGraw-Hill (1963).

35) T. R. Lynn, C. L. Hoffman, and M. M. Austin, Guide to Stationary Phases for Gas Chromatography. Analabs, Inc., Hamden, Connecticut (1968).

36) K. Randerath, Thin Layer Chromatography, Verlag Chemie, Academic Press (1963).

V. ELEMENTS OF INSTRUMENTAL ANALYSIS

In this chapter a brief review is given on principles of selected instrumental methods of chemical analysis. The selected methods are considered applicable for water quality characterization for pollution control. It is realized that there has been no attempt to provide an exhaustive coverage of the subject matter. For more complete coverage the student is referred to textbooks in basic chemistry on instrumental analysis.

A. Chemical Spectophotometry - General

As the name implies, the technique utilizes the absorption of portions of the electro-magnetic spectrum. Figure V-1 illustrates the various portions of the electro-magnetic spectrum. The figure serves to indicate the general areas of the spectrum in spite of the fact that that the boundaries between the various zones are somewhat arbitrary.

The energy in an atom is solely electronic and exists in discrete quantized energy levels. Accordingly, atomic emission or absorption spectra consist of sharp lines of specific spectral wave lengths. On the other hand, the energy of polyatomic molecules consists of electronic energy, involved with the electrons in the atoms; rotational energy, involved with the rotation of a molecule; vibrational energy, resulting from the elastic vibrations of the atoms relative to each other along their internuclear axes. These energies are also quantized, and absorption or emission occurs at specific wave lengths. Nevertheless, these energies are interdependent, so when one type of energy is affected, the other two are also affected. This results in spectra with broad bands at the specific wave Lengths instead of discrete lines.

Absorption in the ultraviolet and visible regions are mainly electronic in nature and are associated with resonating structures in the molecules. In the infrared region, the absorptions are due to the vibrational energies of the groupings in the molecule and the rotational energies of the molecule itself. By observing the absorption characteristics of a chemical material, it is possible to gain information concerning the qualitative nature and quantitative composition of that material.

The optical phenomena and techniques which will be principally discussed in this chapter are:

1. The absorption of radiation by dissolved molecules - Molecular Absorption Spectrophotometry;
2. The absorption-remission of radiation by dissolved molecules - Molecular Fluorescence spectrophotometry;
3. The absorption of radiation by free atoms - Atomic Absorption Spectrophotometry;
4. The absorption-remission of radiation by free atoms, Atomic Fluorescence Spectrophotometry

B. Molecular Absorption Spectrophotometry

The technique is based on the absorption of radiation by molecular species. It is commonly applied for the analysis of metal ions in natural and waste waters and is based primarily on reacting of the metal ions with various organic reagents to form colored compounds which may be determined spectrophotometrically either directly or after appropriate separation. A complexometric reaction between the metal ion and the organic molecule -- acting often as a multi-dentate ligand -- is usually involved.

Although very many organic compounds absorb quite strongly, only a limited number of inorganic ions do, and it is the normal procedure of inorganic absorption spectrophotometry to add a molecule or reagent species to the solution of the inorganic ion which will react with it and, in the process, bring about a marked change in the spectral absorption characteristics of the reagent. It is necessary that the absorption spectrum of the reagent-ion be well separated in at least one place from the absorption spectrum of the reagent itself. It is common practice to add a fairly large excess of the organic reagent so that virtually all of the ionic species are driven to react with the reagent.

Some of the more common organic reagents used for separation by extraction are chelate compounds, e.g., dithizone (diphenylthiocarbazone), oxines, cupferron and diethyldithiocarbamate. Examples of the applications of this technique for analysis of metals in natural and waste waters are given in Table V-1.

TABLE V-1 EXAMPLES OF MOLECULAR ABSORPTION SPECTROPHOTOMETRY FOR METALS IN WASTEWATER

Metal	Complexing Agent	Solvent Extraction	Color of Complex	pH Range	Suitable Wave-Length mu	Useful Range mg/l
Cobalt	Diethyldithio-carbamate	Ethylacetate	blue	acidic pH:3.0	367	---
Cadmium	Dithizone	Carbon-tetra-chloride	red	alkaline pH:10-12	518	0.1-5
Chromium	1.5 diphenyl carbohydrazide	Butanol	violet	acidic pH:2-3	540	0.05-0.5
Copper	Dithizone	Carbon-tetra-chloride	violet	acidic pH:0.5	510	0.04-14
Copper	Diethyldithio-carbamate	Carbon-tetra-chloride	yellow-brown	alkaline pH 9.0	436	0.1-0.8
Copper	Cuprione (2-2'diquinolyl)	Isoamyl alcohol	purple	pH:5-6	540	---
Iron	O-Phenanthroline	----	orange-red	pH:209	490	0.01-1.0

TABLE V-1 (cont.)

Metal	Complexing Agent	Solvent Extraction	Color of Complex	pH Range	Suitable Wave-length mu	Useful Range mg/l
Iron	Thioglycollic acid	----	purple	pH:8-12	540	0.04-1.2
Iron	Tripyridyl	----	red-purple	pH:9-10	560	0.01-2.0
Lead	Dithizone	Chloroform	red	pH:7-10	520	----
Mercury	Dithizone	Carbon-tetra-chloride	yellow-orange	pH:0-1	500	----
Nickle	Dimethylyoxime	----	reddish-brown	neutral	465	----
Zinc	Dithizone	Chloroform	purple-red	pH:4-5.5	530	0.1-1.0
Zinc	Zincon	----	Blue	pH:9.0	620	0.1-2.4

The basic law of absorption spectrophotometry relates the absorbance "A" to the concentration of the absorbing species "C" linearly through the length of the absorbing layer of solution "l" and the molor absorptivity of the absorbing species, "k".

$$A = \log (I_0/I) = klc \qquad (V\text{-}1)$$

where I_0 and I are the intensities of the incident and emitted light respectively. Accordingly, it seems that the analytical signal can be increased for a given concentration of the reacting ion C by increasing the path length l or by using a compound which has a greater molor absorptivity k. This is reasonably true for small changes in l, but the background absorption by other agents in solution becomes limiting for very large light path lengths. Increasing the sensitivity of such determinations ultimately depends on the formation of color compounds of high molor absorptivity.

Sensitivity limits on molecular absorption spectrophotometry for metal analysis is about 10^{-6}M. It is possible, however, to extend this sensitivity by using differential spectrophotometric techniques which also allow for more precise determinations than are possible by conventional procedures. A typical schematic diagram of a double beam optical null balance spectrophotometer is shown in Figure V-2.

C. Molecular Fluorescence Spectrophotometry

Molecular fluorescence spectrophotometry is based on the spectral measurements of fluorescence or phosphorescence radiation emitted from luminescent compounds upon excitation by incident radiation. The reemitted radiation is of lower frequency than the absorbed light. Fluorescence spectra are characteristic of the compound in the sense that the emission spectrum is always the same respective of the wave length of the incident light which promotes fluorescence.

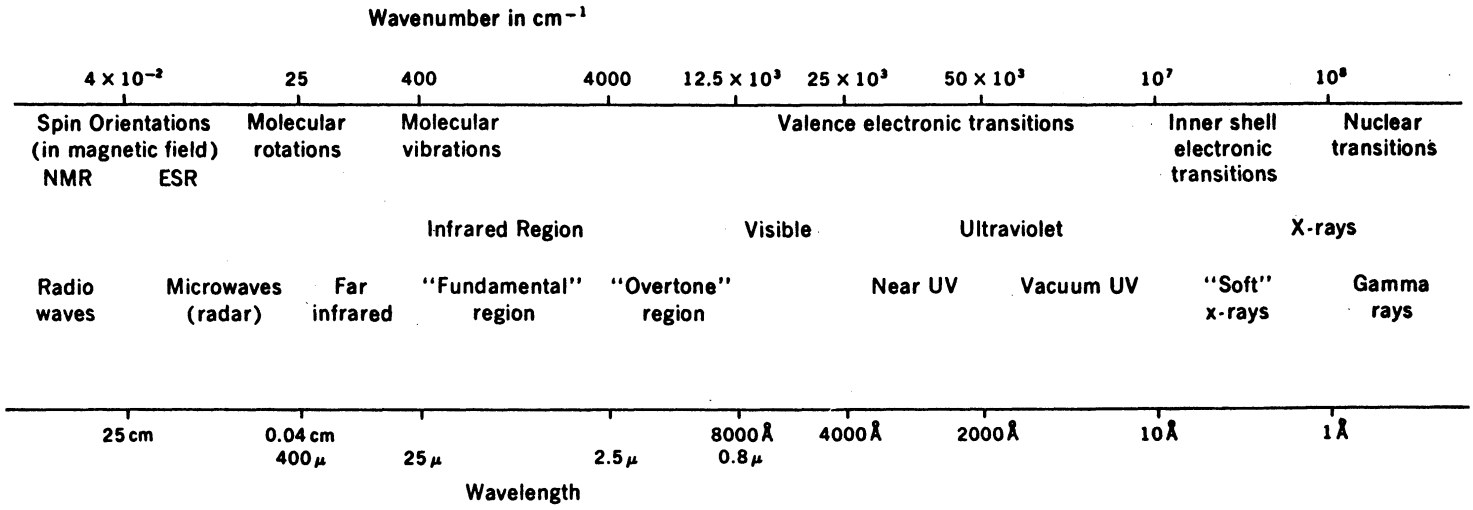


FIGURE V-1 SCHEMATIC DIAGRAM OF ELECTROMAGNETIC SPECTRUM. Note that scale is non-linear. Boundaries between adjacent regions are generally quite arbitrary.

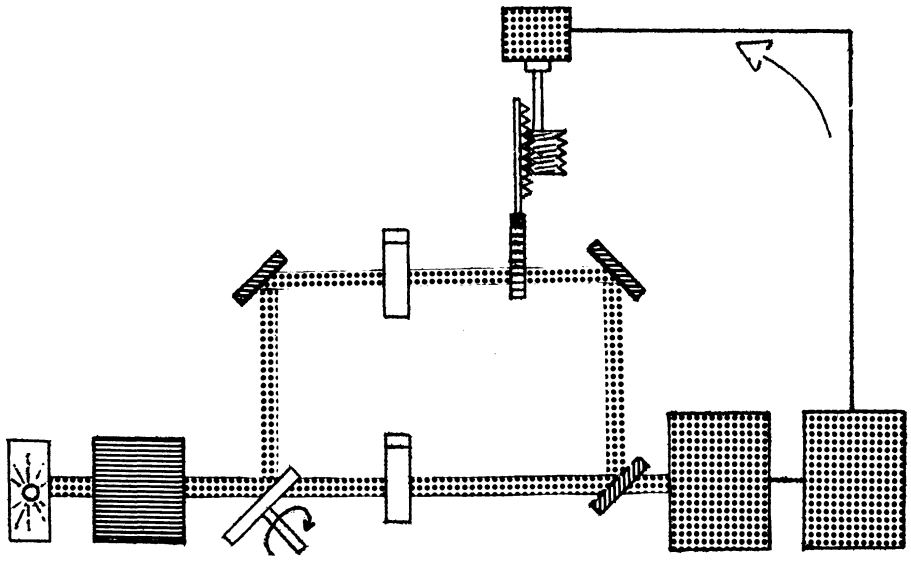


FIGURE V-2 DOUBLE BEAM-NULL BALANCE SPECTROPHOTOMETER

The essential difference between compounds which absorb light and those which absorb and subsequently reemit light is that the latter have unusually stable excited states so that these molecules can retain acquired energy in a definite energy level for a finite time before they dissipate it, and return to the ground state. Only those compounds which have stable excited state configurations will therefore exhibit the phenomenon of resonance radiation, i.e., reemission of photons of the same energy as those originally absorbed which is completely unknown in solutions. Invariably these energetic photons are reemitted by the luminescent compounds so that the fluoresced light has a longer wave length or lower frequency than the absorbed light. The fluorescence is also characteristic of the compound in the sense that the emission spectrum is always the same irrespective of the wave length of the incident light which promotes the fluorescence.

The fluorescence equation may be expressed as follows

$$F = 2.303 \phi I_0 klp C \qquad (V\text{-}2)$$

where F is the amount of fluorescence generated, ϕ is a constant related to the efficiency of fluorescence, I_0 is the intensity of incident radiation, k is the molar absorptivity at a given wave length, l is the path length in centimeters, p is a fractional constant, and C is the concentration. Accordingly, F measured in terms of signal response of a photo-multiplier tube sensitive to fluorescence radiation is proportional to the analytical concentration C, while the parameters I_0, l and p are instrumental factors, and parameters ϕ and k are functions of the efficiency of the fluorescent reagent system.

In the case of absorption spectrophotometry, Equation (V-1), any increase in I_0 will be accompanied by a matching increase in I, with no net gain in the absorbance, A. But, in the case of fluorescence spectrophotometry, any increase in I_0 will be matched by a corresponding increase in the analytical signal F, as indicated in Equation (V-2). It is interesting to note that any in-

crease in the amplifier gain in absorption spectrophotometry will amplify both I_0 and I correspondingly, where as in fluorescence spectrophotometry, this will only result in an increase in F. Accordingly, the sensitivity of molecular fluorescence spectrophotometry is inherently greater than that of molecular absorption spectrophotometry. The technique is extremely useful and is applicable to solutions one hundred to ten thousand times more dilute than those which can be analyzed by absorption spectrophotometry.

The typical instrument used for the analytical application of fluorescence phenomena is shown in Figure V-3. The essential parts are

1. A detector to sense the level of the admitted radiation, usually with an amplifier to enhance the analytical signal,
2. A monochromator or filter system to disperse the fluorescent radiation before it reaches a detector,
3. A cell or cuvette to hold the solution,
4. A monochromator or filter system to disperse the excitation radiation, and
5. A source of radiation of suitable intensity and emission characteristics.

Fluorescence is usually observed at right angles to the instant beam of light to eliminate contamination of fluorescence signals by radiation from the excitation wavelength.

There are a number of fluorometric reagents suitable for analysis of such metals as aluminum, rare earths, zinc, calcium, etc., measurements are based on the extinction of the fluorescence of their reagents with which they react. A typical example of an effective fluorogenic agent is 8-hydroxyquinoline, which forms fluorescent complexes with aluminum, beryllium, etc. and non-fluorescent complexes with iron, copper, etc. Perhaps one of the most desirable characteristics of molecular fluorescence spectrophotometry for the analysis of natural and waste waters is its selectivity. There are only certain ions which are capable of producing fluorescence. For example, few metal ions produce

fluorescence with a non-selective agent like 8-hydroxyquinoline, while over thirty produce absorption spectra.

C. Atomic Absorption Spectrophotometry

Atomic absorption spectrophotometry is a relatively new technique which is gaining great popularity in the analysis of natural and waste waters. The technique is really a combination of emission and absorption phenomena. It closely resembles flame photometry. In flame photometry, a flame excites the elements in the sample to produce an emission spectrum. However, only a small percentage of the atoms are excited. Atomic absorption increases the sensitivity of the flame technique by utilizing the unexcited atoms in the flame. In atomic absorption, as in flame photometry, the sample solution is atomized into a flame, producing atomic vapor of the elements in question. Then monochromatic light from a hollow cathode tube containing the desired element, emitting light of the same wavelengths as that of the desired element) is passed through the atomic vapor of the sample in the flame. The atoms of the desired element, in the vapor, in the flame are mainly in their unexcited or ground state, and they absorb the radiation from the light source. The amount of light absorbed is proportional to the amount of the element in the sample. Hence, the similarity of atomic absorption spectrophotometry to molecular absorption spectrophotometry is based on the fact that atoms are capable of absorbing light in exactly the same way as molecules by interacting with the photons of energy requisite to promote an electronic transition from ground state to one of the excited states of the atom. Hence, the laws which govern the relationship between the amount of light absorbed and the concentration of the absorbing species, as well as the experimental apparatus and techniques, are basically the same for both atomic and molecular absorption spectrophotometry. Figure V-4 shows a schematic diagram of an atomic absorption spectrophotometer.

As an analytical tool, atomic absorption spectrophotometry

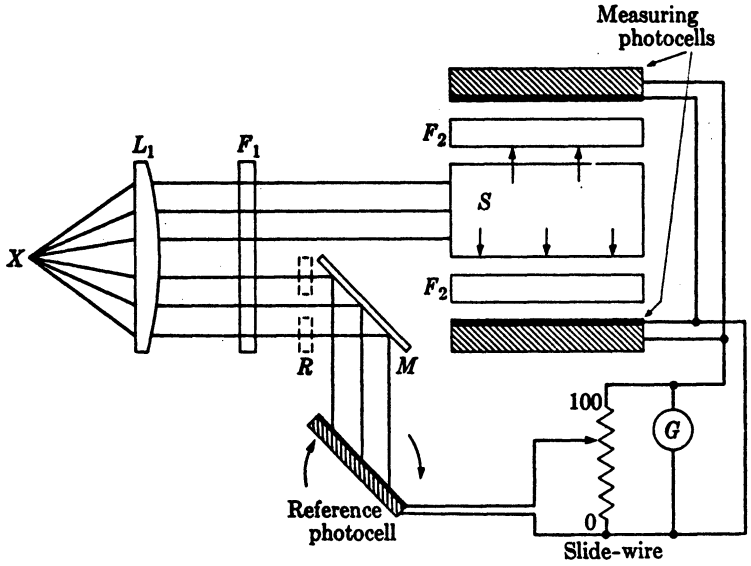


FIGURE V-3 A simplified schematic diagram of a filter fluorometer, the Lumetron Model 402-EF. L_1, collimating lens. F_1, primary filter passing only UV. F_2, secondary filter passing only fluorescent light. R, reduction plate. M, front-surface mirror. G, galvanometer.

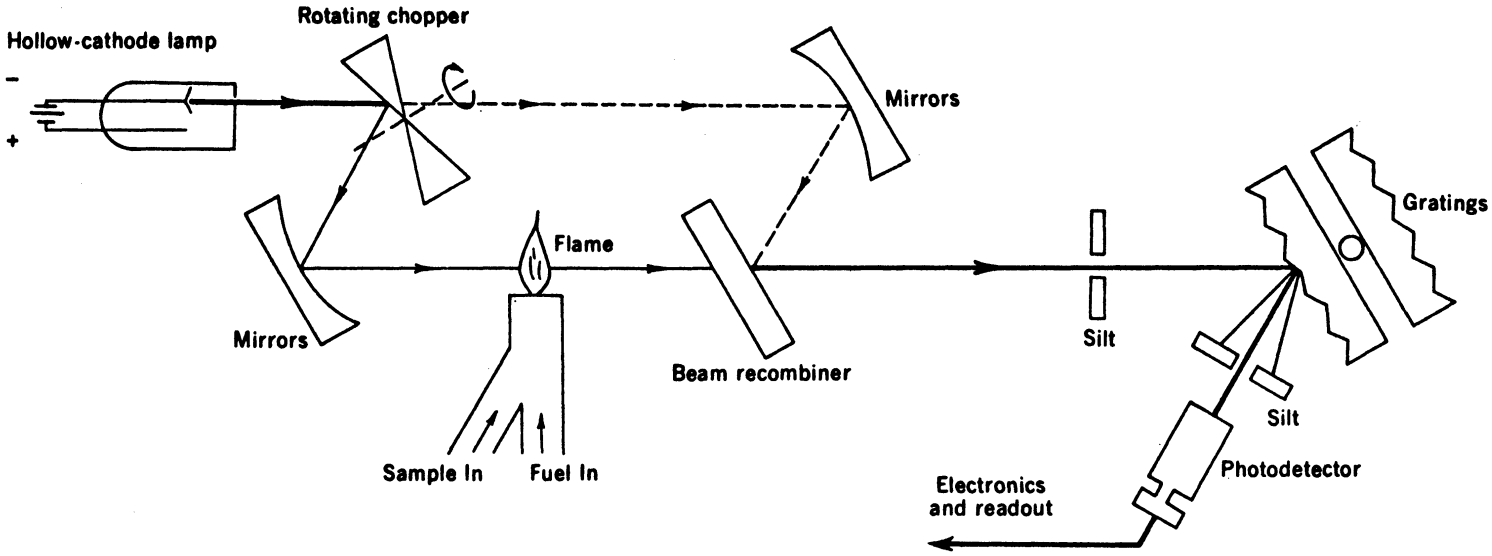


FIGURE V-4 PERKIN-ELMER MODEL 303 ATOMIC ABSORPTION SPECTROMETER.

has the unique advantage of virtual specificity. Exceptions are those few cases in which unfavorable matrix components are present in the sample solution. This is, to a great extent, the result of the presence of certain substances which combine with the metal under analysis to form relatively nonvolatile compounds, which do not break down in the flame. For example, calcium in the presence of phosphate exhibits this effect. This may be remedied by sequestering the calcium ion with EDTA. Matrix effects may be minimized by separation or by adding approximately the same amount of matrix component to the standard solution.

In contrast to flame photometry, there is very little interelement interference in atomic absorption spectrophotometry. In the meantime, while sensitivity in flame photometry is critically dependent on flame temperature, this is not the case for atomic absorption spectrophotometry.

Over sixty elements can be determined readily by atomic absorption in the part per million range without sample pretreatment and with an accuracy of one to two per cent. The sensitivity can be vastly increased to the part per billion range by scale expansion or by extracting the metal in a nonaqueous solvent and spraying it into the flame. This technique finds wide applications in the analysis of various metal species in natural and waste waters. Microgram per liter quantities of cobalt, copper, iron,lead, nickel, and zinc have been determined in saline waters by extraction of metal complexes with ammonium pyrollidine dithiocarbamate into methyl isobutyl ketone. An increase of about sixty per cent in the atomizer efficiency can be achieved with the use of certain organic solvents.

In addition to its selectivity and sensitivity, atomic absorption spectrophotometry is a rapid and easy technique suitable for routine analysis and can be easily automated for monitoring effluent streams and waste water discharges. The detection limits to some common metals are given in Table V-2.

TABLE V-2 ATOMIC ABSORPTION DETECTION LIMITS[1]

Metal	Detection Limit	Analytical Wavelength	Suggested Resolution
Silver	0.005	3281	7A.
Aluminum[2]	0.1	3093	2A.
Arsenic[3]	0.1	1937	7A.
Boron[2]	6.0	2497	7A.
Barium[2]	0.05	5536	4A.
Beryllium[2]	0.002	2349	20A.
Bismuth	0.05	2231	2A.
Calcium	0.002	4227	13A.
Cadmium[3]	0.001	2288	7A.
Cobalt	0.005	2407	2A.
Chromium	0.005	3579	2A.
Copper	0.005	3247	7A.
Iron	0.005	2483	2A.
Mercury	0.5	2537	20A.
Potassium	0.005	7665	13A.
Lanthanum[2]	2.0	3928	4A.
Lithium	0.005	6708	40A.
Magnesium	0.0003	2852	20A.
Manganese	0.002	2795	7A.
Molybdenum	0.03	3133	2A.
Sodium	0.002	5890	4A.
Nickel	0.005	2320	2A.
Lead	0.03	2833	7A.
Antimony	0.1	2175	2A.
Selenium[3]	0.1	1961	20A.
Silicon[2]	0.1	2516	2A.
Tin[3]	0.02	2246	7A.
Tellurium	0.1	2143	7A.
Titanium[2]	0.1	3643	2A.
Thallium	0.025	2768	20A.
Vanadium[2]	0.02	3184	7A.
Tungsten[2]	3.0	4008	2A.
Zinc	0.002	2138	20A.
Zirconium[2]	5.0	3601	2A.

[1] The detection limit is given by the metal concentration in ppm which gives a signal twice the size of the peak to peak variability of the background.

[2] Nitrous oxide flame required.

[3] Indicates use of argon-hydrogen flame.

E. Atomic Fluorescence Spectrophotometry

It appears from the above discussion that molecular fluorescence spectrophotometry offers distinct advantages of greater sensitivity and selectivity over molecular absorption spectrophotometry. Relative to atomic absorption spectrophotometry, however, no increase in selectivity can be gained by using atomic fluorescence since the former is virtually specific for each element. Nevertheless, it is possible to increase the sensitivity of measurements with atomic fluorescence spectrophotometry by increasing the intensity of irradiation or by increasing the amplification until the system becomes noise limited. In this sense, atomic fluorescence spectrophotometry offers greater flexability and sensitivity than atomic absorption spectrophotometry.

The analytical relationships in atomic fluorescence spectrophotometry can be simply given by the following equation

$$F = k\phi I_o C \qquad (V\text{-}3)$$

where k is a constant specific for a given atomizer and instrumental set of conditions. From Equation (V-3), the fluorescence signal is proportional to the intensity of irradiation and to the concentration of the preatomic species in the solution. A schematic diagram of an apparatus for atomic fluorescence spectrophotometry is given in Figure V-5.

The technique is inherently simple and practically any flame spectrophotometer may be adapted for this purpose without interference with its normal mode of operation. A continuous source with simple monochromator may be used. Where high sensitivities in the subnanogram range are required, it is necessary to use individual spectro discharge lamps.

F. Infrared Absorption Spectrophotometry

This technique is essentially a molecular absorption spectro-

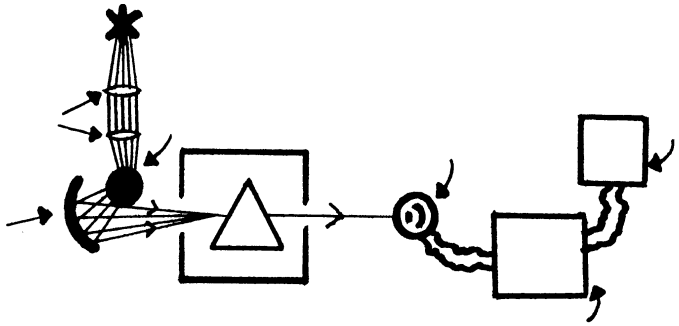


FIGURE V-5 APPARATUS FOR ATOMIC FLUORESCENCE SPECTROPHOTOMETRY

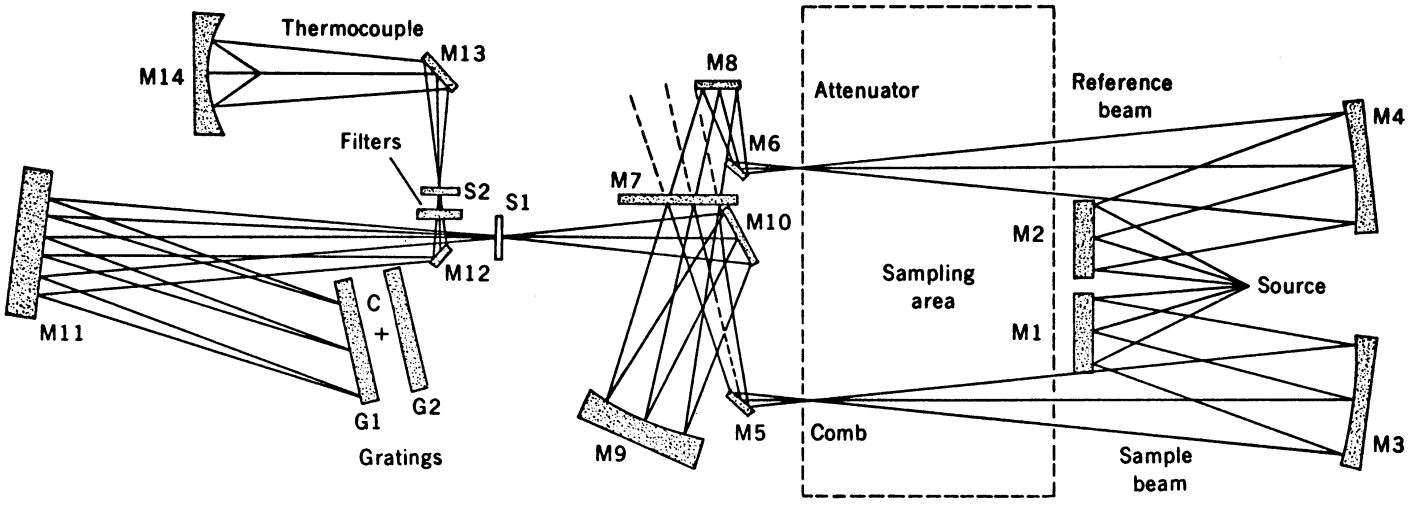


FIGURE V-6 PERKIN-ELMER MODEL 621 INFRARED SPECTROMETER

photometric procedure. This involves the dispersing of a polychromatic infrared beam of light using a suitable prism or defraction grating. Narrow wavelength bands of infrared light are isolated by a slit and allowed to pass through the sample. The analysis is run by passing the polychromatic light through the sample, which absorbs portions of the light. The remaining light then passes through a prism or grating where it is dispersed into its component wavelengths. The resultant spectrum is scanned by a detector which records the intensity at each wave length. Figure V-6 shows a schematic diagram of an infrared analyzer. The sample solution will preferentially absorb specific wave lengths of the radiation depending on the vibrational and rotational energies of the bonds in the molecule. Various functional groups, composed of definite atomic configurations with definite vibrational and rotational energies, absorb strongly at characteristic wavelengths. Accordingly, infrared absorption analysis provides a very useful tool for the characterization of organic compounds by means of functional group analysis.

Only a few solvents can be used in infrared analysis since most solvents absorb infrared so strongly. This can be seen by examining the infrared absorption chart given in Figure V-7.

Interpretation of infrared spectra is rather a complicated process. There are several factors which can influence the spectra and which must be taken into account in interpretation and detection of functional groups. Substitutions and molecular symmetry will shift functional group absorption locations and will affect the intensity of the absorption bands. For example, the absorption for the triple bond in acetylenic molecules is intense for asymmetric molecules, but is weak for symmetrical molecules. In the meantime, sample crystallinity, solute-solvent, and solute-solute interaction will all affect the appearance of the spectrum. Also, if the sample is prepared in solution, as a mineral oil (Nujol) mull or as a potassium bromide pellet or if the pure sample is presented to the instrument, different spectra for the same material can result.

The infrared spectrum in the range between 0.7 μ to 2.5 μ provides unique analytical possibilities. This is referred to,

generally, as near infrared absorption spectrophotometry. This region is primarily concerned with overtone vibrations, and thus the absorption bands are generally weaker than those in the rest of the infrared region.

The difference between near and conventional infrared instrumentation is that with near infrared an ordinary incandescent light source can be used, in addition, quartz optics (or defraction gratings) and also quartz cells for handling liquids can be used along with lead sulfide detectors. Conventional infrared covers the range between 2.5 μ to 15 μ and requires a source of infrared radiation, crystal optics (sodium, potassium, cesium, calcium, berylium or silver halides, or sapphire), and bolometer or thermocouple detectors.

In spite of the fact that the analytical utility of the near infrared region is limited because of few absorption peaks, it can be readily used to determine hydroxy compound such as alcohols, phenols and carboxyllic acids as well as hydrazines, imines and similar compounds as shown in Figure V-8.

With reasonable care, it is feasible to reproduce absorptivities within approximately 0.5% when employing the same sample cell and spectrophotometer. Infrared analysis of natural and waste waters is primarily used for the identification of organic compounds. The technique is usually applied after a preliminary separation procedure, such as gas chromatography or liquid-liquid extraction.

G. Ultraviolet Absorption Spectrophotometry

The principle of operation of ultraviolet absorption spectrophotometry is similar to that of the infrared technique except that a polychromatic ultraviolet light source is used. Also, in the case of ultraviolet spectrophotometers, the prism or defraction grating is placed before the sample so that only narrow wave length bands pass through the sample, as is done with infrared, the large ultraviolet input of energy could cause fluorescence to occur which could confuse the spectrum. Furthermore, large amounts of ultraviolet energy could cause photochemical reactions to occur

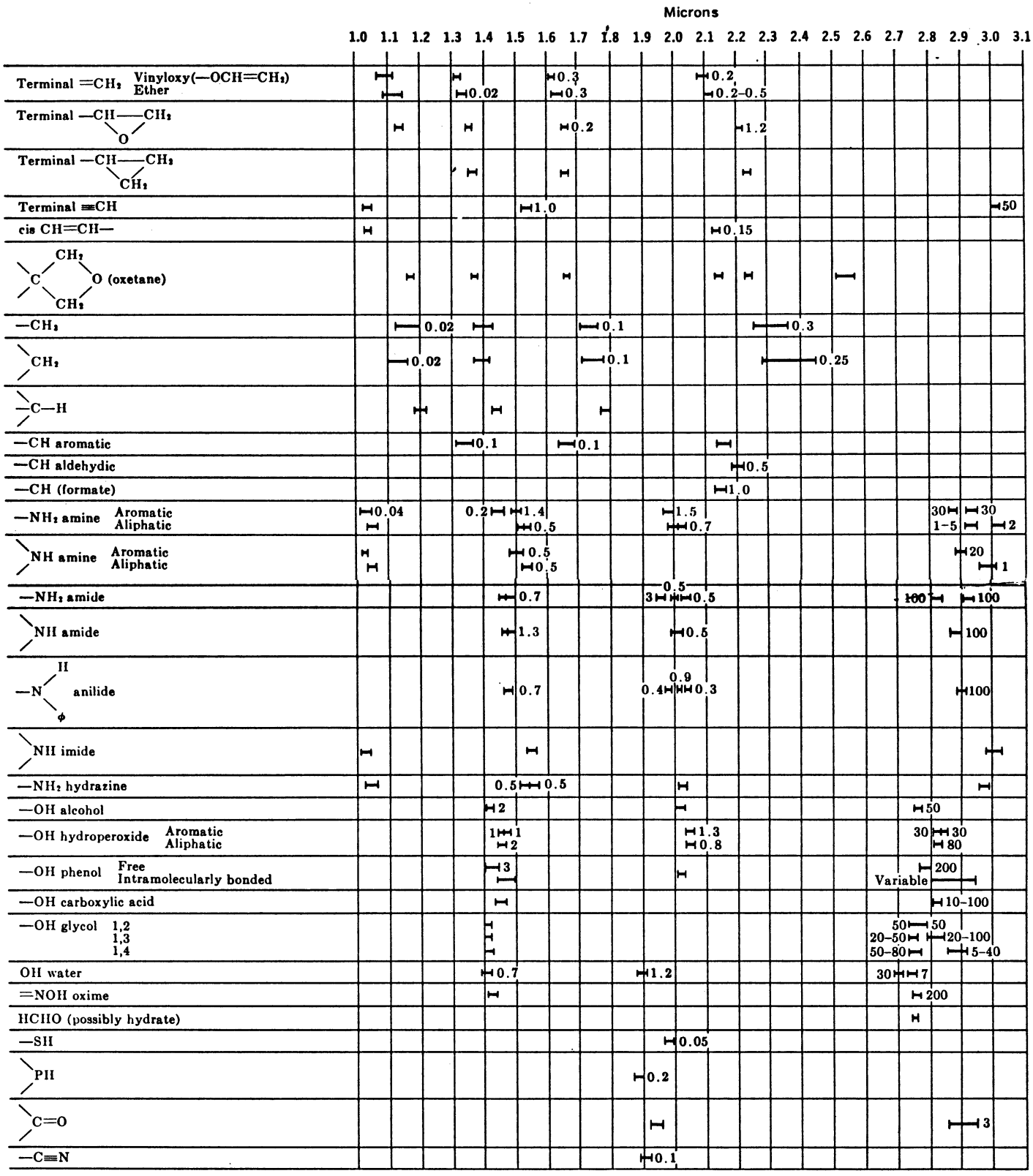
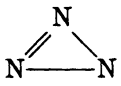
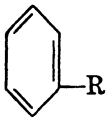
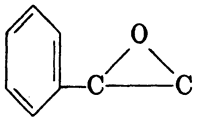
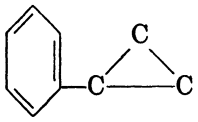
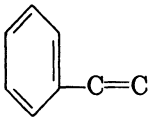
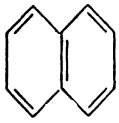
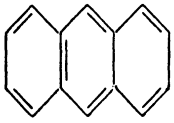


FIGURE V-8 SPECTRA-STRUCTURE CORRELATIONS AND AVERAGE MOLAR ABSORPTIVITY DATA FOR NEAR-INFRARED REGION

* Published data, mostly obrained in CCl_4 solution. Units are liter/mole-cm.

Group	Absorption, mμ	Conjugation	Absorption, mμ
N=N	350		288
	259		260
			274
			290
	311		
	475		

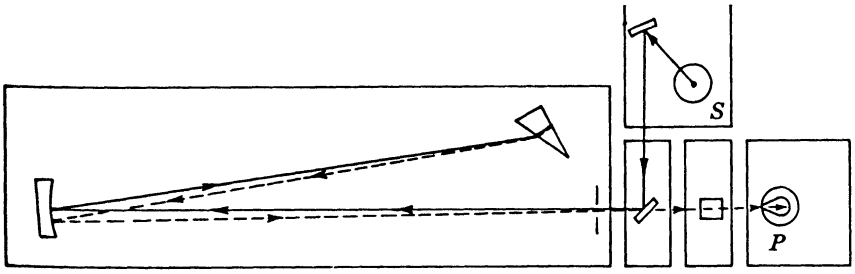


FIGURE V-9 ULTRAVIOLET ABSORPTION OF CHRONIPHORIC GROUPS-SCHEMATIC OF D.V. BECKMAN SPECTROPHOTOMETER

with some materials. A simple diagram of an ultraviolet spectrophotometer is shown in Figure V-9 in contrast to infrared technique, in the ultraviolet range only few atomic configurations in the molecules absorb. Those that do absorb do not have to be functional groups but rather highly resonating molecular configurations. The energy involved is due to electron transitions from one state to another. Typical examples are conjugated saturated bonds, aromatic system with their conjugated cyclic structures as shown in Figure V-9.

Also, different from infrared spectra, ultraviolet absorption spectra are generally much simpler to interprete. This is due to few absorption peaks. These can be used to get some idea of the class of the compound but cannot be used to give conclusive information. UV absorption technique is more applicable in cases of compounds of highly conjugated bonds such as the aromatics, where several absorption peaks exist. The precision and accuracy of quantitative ultraviolet analysis can be generally obtained in the range of 0.5-2% at the maximum sensitivity.

H. Electrochemical Analysis

Electrochemical methods are often well suited for metal ion analysis in natural waters and wastewaters. A variety of electrode systems and electrochemical techniques have been used routinely for *in situ* analysis and continuous monitoring of waste effluents.

For purposes of this discussion, electrochemical methods are conveniently classified as being either based on the passage of a faradaic current - e.g., classical polarography - or based on electrode equilibrium - e.g., potentiometry.

Classical polarography has been used widely for water analysis since its development. Polarographic measurements are based on determining the time-averaged currents of the dropping mercury electrode under diffuion conditions. The response is described approximately by the Ilkovic equation,

$$i_d = [605\ n\ D^{1/2}\ m^{2/3}\ t^{1/6}]\ C \qquad \text{(V-4)}$$

where: i_d is the average diffusion current (μ amp); t is the drop-time (sec); m is the mass rate of flow of mercury (mg/sec); D is the diffusion coefficient of the electroactive species (cm^2/sec); C is the concentration of electroactive species (millimoles per liter); and n is the number of electrons per molecule involved in the electrode reaction. For a typical case in which m = 2 mg/sec, t = 4 sec, and D = 10^{-5} cm^2/sec, the electrode response will be i_d/C = 3.82 μ amp/millimole/liter.

As a result of the capacitance current used in charging the double layer, the sensitivity of classical polarography with the dropping mercury electrode is limited to approximately 10^{-5} *M*.

However, by means of preconcentration techniques it may be possible to extend the sensitivity range significantly. Copper, bismuth, lead, cadmium, and zinc have been measured in the range of 0.01 mg/liter after extraction with dithizone and carbon tetrachloride. (1) Preconcentration by ion exchange, freeze drying, evaporation, or electrodialysis may be used.

A significant problem is the application of classical polarography to industrial wastewater analysis is the interference produced by electroactive and surface active impurities. Such impurities, frequently present in wastewaters, may interfere with electrode reaction processes and cause a suppression and/or a shift of the polarographic wave. (2)

Modifications of polarographic techniques, such as "differential polarography" and "derivative polarography," may be used to increase the sensitivity and minimize the effect of interferences. (3) Pulse polarography has the advantage of extending the sensitivity of determination to approximately 10^{-8} M. The technique is based on the application of short potential pulses of 50 msec on either a constant or gradually increasing background voltage. Following application of the pulse, current measurements are usually done after the spike of charging current has decayed. The limiting current in pulse polarography is larger than in classical polarography. The diffusion current equation for pulse polarography is as follows:

$$i_d = [n\ F\ A\ (\frac{D}{t})^{0.5}\ ]\ C \qquad \text{(V-5)}$$

Derivative pulse polarography, which is based on superimposing the voltage pulse upon a slowly changing potential (about 1mv/sec) and recording the difference in current between successive drops versus the ptential, is even more sensitive than pulse polarography.

Cathode-ray polarography or oscillographic polarography has been used for analysis of natural waters and wastewaters, with a sensitivity of 10^{-7}M being reported. (4, 5, 6) This technique involves the use of a cathode-ray oscilloscope to measure the current-potential curves of applied (saw-tooth) potential rapid sweeps during the lifetime of a single mercury drop. Multiple sweep techniques are also applicable. The peak current (i_p) in the resulting polarogram is related to the concentration of the electroactive species for a reversible reaction in accordance with the following relationship:

$$i_p = [k\ n^{3/2}\ m^{2/3}\ t^{2/3}\ D^{1/2}\ v^{1/2}]\ C \qquad \text{(V-6)}$$

where $v = \frac{dE}{dt}$ is the voltage sweep (about 6000 v/min.).

Oscillographic polarography has the advantages of: (a) relatively high sensitivity; (b) high resolution; and (c) rapidity of analysis. Traces of Cu, Pb, Zn and Mn can be determined at 0.05 mg/ml level in natural waters by this technique. (5)

One of the most interesting electrochemical approaches to metal analysis in trace quantities is anodic stripping voltammetry. (7) This technique involves two consecutive steps: (a) the electrolytic separation and concentration of the electroactive

species to form a deposit or an amalgam on the working electrode; and (b) the dissolution (stripping) of the deposit. The separation step, best known as the pre-electrolysis step, may be done quantitatively or arranged to separate a reproducible fraction of the electroactive species. This can be done by performing the pre-electrolysis step under carefully controlled conditions of potential, time of electrolysis, and hydrodynamics of the solution.

The stripping step is usually done in an unstirred solution by applying a potential - either constant or varying linearly with time - of a magnitude sufficient to drive the reverse electrolysis reactions. Quantitative determinations are done by integrating the current-time curves (coulometry at controlled potential) or by evaluating the peak current (chronoamperometry with potential sweep). Several modifications of the separation and stripping steps have been reported. (8)

Hanging-drop mercury electrodes of the Gerischer's type (9) or of Kemula's type (10) have been widely used for anodic (or cathodic) stripping analysis. Greater sensitivity has been achieved by use of electrodes which consists of a thin film of mercury on a substrate of either platinum, silver, nickel, or carbon. (11) Errors due to non-faradaic capacitance current components can be minimized by proper choice of stripping technique.

The main advantage of stripping voltammetry is its applicability to trace analysis. The technique has been applied for metal analyses in sea water, (12) natural waters (13, 14) and wastewaters. (13)

Electroanalytical methods based on,electrode equilibrium include a variety of membrane electrode systems which are applicable for analyses of metals in natural waters and wastewaters.

Recent developments in glass electrodes make it possible to use these electrodes to analyze for certain metal ions, particularly sodium and potassium. (15) The doping of ordinary glass pH electrodes with Al_2O_3 greatly enhances the "alkaline error" or the response of these electrodes to alkalies, although at the same time reducing their pH response.

It has been found experimentally (15) that for a mixture of two cations, e.g., Na^+ and K^+, the behavior of a modified glass electrode may be described by a modified form of the Nernst equation.

$$E = \text{const.} + RT/F \ln [a_{A+} + K\, a_{B+}] \qquad \text{(V-7)}$$

where a_{A+} and a_{B+} are the activities of A^+ and B^+ ions, respectively, and K is a selectively constant which expresses the relative sensitivities of the glass electrode for ions B^+ and A^+. By varying the composition of the glass in the system $M_2O \cdot Al_2O_3 \cdot SiO_2$ - where M_2O is either Li_2O, Na_2O, K_2O, Rb_2O or Cs_2O - it is possible to vary the selectivity of response of the glass to each of the various alkali metal ions.

Liquid ion exchange has been used in conjunction with potentiometric specific-ion electrode systems. One example is the calcium-selective membrane electrode, (16) which consists of the calcium salt of dodecylphosphoric acid dissolved in di-n-octylphenyl

phosphate. This liquid ion-exchanger is immobilized in a porous inert membrane such as cellulose. Below a solution concentration of 10^{-6} moles Ca^{+2} per liter, the membrane potential is a constant, independent of the calcium ion activity. This has been attributed to the organic calcium salt solubility, which maintains a constant limiting activity of calcium ions at the membrane solution interface. (16, 17) Otherwise, the liquid ion exchange membrane electrode exhibits behavior similar to that of the glass electrode, which may be expressed in terms of the modified Nernst relationship given in Equation

Single crystal membrane electrode systems (solid-state membrane electrodes) have been recently applied to water analysis. (18, 17) The fluoride electrode, (18) which is made of lanthanum fluoride crystal membrane doped with a rare earth which presumably acts so that only fluoride carries current across the membrane, is a good example. This electrode system is highly selective for fluorides, but, at high pH, hydroxide ions constitute a major interference which limits its usefulness in this range. The introduction of anion selective, precipitate-impregnated, membrane electrodes (19, 20) has been an important recent development for electrochemical analytical techniques. The membrane is made of a silicone rubber matrix which incorporates precipitated particles of silver halide, or barium sulfate. The electrode is relatively unsensitive to the nature of the cations. The most selective and sensitive electrode system of this type is the silver iodide membrane electrode which responds to iodide concentrations as low as 10^{-7} M, with relatively little interference from common ions. (20)

Although the last two membrane electrode systems described above are not sensitive to metal ions, they are included in this section to provide a unified coverage of potentiometric membrane electrodes.

From Equation it is apparent that potentiometric membrane electrode systems are sensitive to the activity of the electroactive species. In order to use such electrode systems for determination of concentrations rather than activities, it is important to consider the effects of ionic strength on the activity coefficient of the electroactive species and the liquid junction potential between the test solution and the reference electrode. To avoid the uncertainty of estimating an activity coefficient, it is useful to determine the effect of an added known amount of species on the potential, or adjust the ionic strength of the sample to that of a standard solution. Since the total ionic strength of the solution determines the activity coefficient for a specific ion, the activity coefficient of the ion being analyzed in the test sample will be identical to that in the standard solution. A constant ionic strength can be obtained by using a "swaming electrolyte." This technique, frequently referred to as the "ionic medium" method, has been effectively used to calibrate potentiometric membrance electrode systems for the analysis of natural waters and wastewaters. (17, 21)

The literature contains conflicting reports regarding the sensitivity limits for the various electroanalytical procedures discussed herein. A helpful discussion of this subject has been given by Laitinen; (22) the conclusions of this discussion are in Table V-3. The sensitivity values given in Table XII are

TABLE V-3 QUANTITATIVE SENSITIVITY LIMITS OF SOME ELECTROANALYTICAL METHODS

Methods	Sensitivity Limit, M
AC polarography; chronopotentiometry; thin layer coulometry; potentiometry with metal-specific glass or membrane electrodes.	10^{-4}–10^{-5}
Classical polarography; coulometry at controlled potential; chronocoulometry; tensammetry; precision null-point potentiometry.	10^{-5}–10^{-6}
Test polarography; derivative polarography; square-wave polarography; second harmonic AC polarography; phase-sensitive AC polarography; linear sweep voltammetry; staircase voltammetry; derivative voltammetry; coulostatic analysis; chemical stripping analysis.	10^{-6}–10^{-7}
Pulse polarography; RF polarography; coulometric titrations; amperometry with rotating electrodes; conductivity (aqueous).	10^{-7}–10^{-8}
Anodic stripping with hanging mercury drop electrodes	10^{-7}–10^{-9}
Anodic stripping with thin film electrodes or solid electrodes	10^{-9}–10^{-10}

defined as the lowest concentrations at which a determination can be made with a relative precision of 10% in the presence of a large concentration of major constituents. (22)

A complete analysis of metal ions in natural waters and wastewaters should include definition of oxidation states and characterization of aquometallic or organometallic complexes. Aquometallic complexes in natural waters and wastewaters undergo exchange reactions in which coordinated water molecules are exchanged for certain organic ligands. The pH and the concentration of the organic ligands are important factors affecting such coordination reactions.

Electrochemical methods, in general, are more suited for elucidation of the oxidation state and complexed form in which metal ions exist in a particular sample than are spectrophotometric analyses. Organic polarography, in one or more of the various modes discussed previously, provides a useful method for such determinations. Recent studies have demonstrated the analytical feasibility of thin layer anodic stripping voltammetry for the quantitative estimation of free and bound metals in natural waters. (23)

Membrane electrodes, either of the voltammetric or the potentiometric type, are usually sensitive only to free or unbound metal ions in a water sample. For example, in one case in which the calcium membrane electrode was used in a sea water sample, only 16% of the total calcium content was detected; (24) the authors explained this in terms of the remainder of the calcium being complexed with sulfates and/or carbonates.

Future prospects for metal ion analyses in waters and wastewaters include the use of gas chromatography and NMR techniques. It would appear that more emphasis will be placed on the characterization of organometallics in wastewaters than on elemental analysis *per se*.

Selected Specific References

Electrochemical Analysis

1. Heller, K., G. Kuhla, and F. Machek, Mikrochemie, 18, 193 (1935).
2. Mancy, K.H., and D.A. Okun, Anal. Chem., 32, 108 (1960).
3. Schmidt, H., and M. von Stackelbert, "Modern Polarographic Methods," Academic Press, New York)1963).
4. Pohl, F.A., Z. Anal. Chem., 197, 193 (1963).
5. Whitnack, G.C., J. Electroanal. Chem., 2, 110 (1961).
6. Hetman, J., J. Applied Chem., 10, 16 (1960).
7. Shain, I., and S.P. Perone, Anal. Chem., 33, 325 (1961).
8. Shain, I., "Stripping Analysis," in Kolthoff and Elving's Treatise on Analytical Chemistry, Part I, Vol. 4, pp. 50, Interscience Publishers, (1959).
9. Gerischer, H., Z. Physik. Chem. (Leipzig), 202, 302 (1953).
10. Kemula, W., A. Kublick, and Z. Galus, Nature, 184, 1795 (1959).
11. Matson, W.R., D.K. Roe, and D.E. Carritt, Anal. Chem., 37, 1954 (1965).
12. Ariel, M., and U. Eisner, J. Electroanal. Chem., 5, 362 (1963).
13. Maienthal, E.J., and J.K. Jaylor, "Polarographic Methods in Determination of Trace Inorganics in Water," in Gould's Trace Inorganics in Water, Advances in Chemistry Series, American Chemical Society, Vol. 73, pp. 172 (1968).
14. Macchi, G., J. Electroanal. Chem., 9, 920 (1965).
15. Eisenman, G., in Reilley's Advances in Analytical Chemistry and Instrumentation, Vol. 4, Interscience (Wiley), pp. 213 (1965).

16. Ross, J.W., Science, 156, 1378 (1967).

17. Andelman, J.B., Proc. 140th Annual Conference, Water Pollution Control Federation, Washington, D.C. (1967).

18. Frant, M.S., and J.W. Ross, Science, 154, 1553 (1966).

19. Pungor, E., K. Toth, and J. Havas, Acta Chim. Acad. Sci. Hung., 41, 239 (1964).

20. Rechnitz, G.A., M.R. Kiesz, and S.B. Zamochnick, Anal. Chem., 38, 973 (1966).

21. Sillen, L.G., "Master Variables and Activity Scales," in Gould's "Equilibrium Concepts in Natural Water Systems," Advances in Chemistry Series No. 67, American Chemical Society, Washington, D.C. (1967).

22. Laitinen, H.A., "Trace Characterization by Electrochemical Methods," in Trace Characterication - Chemical and Physical, NBS Monograph 100, pp. 75 (1967).

23. Allen, H., W.R. Matson, and K.H. Mancy, J. Water Pollution Control Federation, in press.

24. Thompson, M.E., and J.W. Ross, "Calcium in Sea Water by Electrode Measurement," Science, 154, 1643 (1966).

SELECTED REFERENCES

Molecular Absorption Spectrophotometry

1) Charlot, G. "Colorimetric Determination of Elements" Elsevier Publishing Company, Amsterdam (1964).

2) Willard, Merritt and Dean, "Instrumental Methods of Analysis" 4th Ed., D. van Norstrand Co., Inc., Princeton, N.J. (1960).

3) Meites and Thomas, "Advanced Analytical Chemistry", McGraw-Hill Book Company, Inc., New York (1958).

Molecular Fluorescence Spectrophotometry

1) Radley, J. A. and Grant, J., Fluorescent Analysis in Ultraviolet Light, 4th Ed., D. van Norstrand Co., Inc., Princeton, N.J. (1954).

2) Strobel, H. A., "Chemical Instrumentation", Addison-Wesley Publishing Co., Inc., Reading, Mass. (1960).

Atomic Fluorescence Spectrophotometry

1) Alkemade, C. T. "Xth Colloquium Spectroscopicum Internationale Proceedings", E. R. Lippincott and M. Margoshes, Editors, Sparton Books, Washington, D.C. (1963).

2) Winefordner, J. D., Parsons, M. L., Mansfield, J. M., McCarthy, W. J., Anal. Chem., 39, 436 (1967).

3) ibid, Spectrochim. Acta, 23B, 37 (1967).

Atomic Absorption Spectrophotometry

1) Elwell, W. T. and Gidley, A. F. "Atomic Absorption Spectrophotometry" The Macmillan Co., New York (1962).

2) Robinson, J. W. "Atomic Absorption Spectroscopy", Marcell Dekker, Inc., New York (1966).

Infrared Spectrophotometry

1) Bellamy, "The Infrared Spectra of Complex Molecules" John Wiley & Sons, Inc., New York (1958).

2) Mellon, "Analytical Absorption Spectroscopy" John Wiley & Sons, New York (1950).

3) Szymanski, H. A. "Infrared Handbook" Plenum, New York (1962).

Ultraviolet Spectrophotometry

1) Shriner, Fuson and Cartin, "The Systematic Identification or Organic Compounds" John Wiley & Sons, Inc., New York (1956).

2) Brande and Nachod "Determination of Organic Structures by Physical Methods" Academic Press, Inc. New York (1955).

Electrochemical Analysis

1) Milazzo, G. "Electrochemistry" Elsevier Publishing Co., Amsterdam (1963).

2) Charlot, G., Badoz-Lambling, J. and Tremillon, B. "Electrochemical Reactions" Elsevier Publishing Co., Amsterdam (1962).

3) Reilley, C. N. and Murray, R. W. "Electroanalytical Principles" Interscience Publishers, New York (1963).

VI. CONTINUOUS MONITORING SYSTEMS

The development of equipment capable of continuous monitoring and remote sensing of the environment greatly extends man's capability to understand and control water resources. The number of grab samples which can be collected and analyzed is small. Continuous monitoring equipment provides analyses at short time intervals on a 24 hour basis. Systems for continuous monitoring are generally located at a fixed position on a stream in a permanent building or in a trailer. Therefore, the excellent coverage of fluctuations in water quality by these continuous monitoring systems will often need to be coupled with sampling programs to define the types of wastes being introduced and their dispersion characteristics. Two types of continuous monitoring systems will be discussed; (1) systems which make measurements after suitable chemical reactions have taken place (e.g. Technicon CSM 12) and (2) systems which make measurements without chemical modification of the sample (e.g. Honeywell W-20 system).

A. Technicon Systems

The Technicon AutoAnalyzer described in Chapter VII can be used for continuous analysis by elimination of the sampler module. The sample may be provided by placing the line for the sample pump tube directly into the stream to be sampled. If this would require an excessive length of tubing, laminar flow in the tubing will prevent the measurement of abrupt concentration changes. This condition will exist in oceanographic studies when samples from great depths are to be analyzed or where the analyzer must be located at some distance from the stream. In these cases a separate high velocity pump should be used to provide the water to a small reservoir from which the AutoAnalyzer pump can withdraw a sample. A sampler for oceanographic use which segments the sample with air has been described (2). Armstrong and LaFond (1) show the results of continuous silicate and nitrate analyses off the coast of California.

Frequently continuous analyses for several constituents are

desired. Large numbers of AutoAnalyzers are not only expensive but require a large amount of space to operate. Two new instruments, the Continuous Simultaneous Monitors CSM6 and CSM12, are designed for the measurement of six or twelve components. Their proportioning pumps operate at a slower speed than those for the regular AutoAnalyzer permitting unattended operation for a long time. A single colorimeter which contains a flow cell and photocell for each determination and one reference photocell is used. A programmer sequentially allows the individual measurements to be recorded on a single strip chart recorder. The programmer periodically allows a standard solution to be sampled to maintain calibration unattended for at least one week and can easily be installed in a trailer to permit ease in mobility and allow monitoring at virtually any desired location.

B. Honeywell System

While the Technicon systems described above automate wet chemical procedures, the Honeywell system is designed to measure automatically and record water quality parameters which are measured by instrumental methods. These measurements include pH, conductivity, temperature, dissolved oxygen (D.O.), turbidity, oxidation-reduction potential (ORP), and chloride.

The Honeywell W-20 system is portable and designed for virtually unattended operation. The system consists of a recording module, and a mounting base. The modules can easily be moved and assembled at the location to be monitored. As with the Technicon system, the Honeywell W-20 may be mounted in a trailer for convenient movement from one location to another. Such a mobile facility for either unit will require a generator to provide the necessary power or its use will be limited to locations where electrical power is nearby.

A continuous flow of sample is provided to the sensors by a submersible pump. By using a submersible pump with a minimum flow of 10 gallons per minute, water is pushed through the piping and into the sample tank. Care must be taken to assure that no air pockets are present or dissolved oxygen and other measurements will be unreliable. The sample intake should be shielded with a screen to

prevent debris from clogging the system or damaging the pump. Flexible hose should be used to connect the pump and sample tank for temporary installations while rigid pipe may be used at permanent sites.

The sampling and sensor module holds the conductivity, D.O., temperature, ORP, pH, and chloride sensors. Water is distributed to individual measuring chambers which are made of copper to inhibit algal growths. A high flow is presented across the face of the dissolved oxygen electrode to provide optimum response while in the other chambers, polyethylene baffle cones prevent build-up of particulate matter by agitation of the heavy particles into the overflow drain.

Each sensor in the instrument is supplied with its own signal conditioner which converts the input to a 4-20 mamp D.C. output. Calibration of the sensor signals is accomplished by adjustment of the controls on the signal conditioner. For the dissolved oxygen, temperature, and turbidity sensors the ElectriK Tel-O-Set MV/I serves as a signal conditioner. This unit has an adjustable input span of 2.5 to 100 mv D.C. and converts the input voltage to a 4 to 20 mamp output. Chloride, pH, and ORP sensors use amplifier units to produce the necessary 4 to 20 mamp output and a servo amplifier circuit is used for the conductivity measurement. Water level changes act on a thin disphragm to change the internal pressure which is then converted to a millivolt output by the PP/I transmitter.

C. Data Collection

The Honeywell W-20 monitoring system is generally used with a multipoint recorder to record the data. These data often must be transcribed to permit further analysis such as the computation of the average. In many applications, it is necessary to obtain the information immediately so that remedial action can be taken. The sheer bulk of data which can be obtained from a monitoring system requires the use of supplemental means of data acquisition. An eight parameter system, for example, generates 5376 data points per week if each channel is monitored on a fifteen minute cycle.

Supplemental data acquisition can be local or the data can be telemetered to a remote location. Telemetering of either digital or analog data is possible. Analog transmission, accomplished by variation of the frequency of the signal, requires less expensive equipment than that for digital transmission, but there is a loss in accuracy during transmission of the data. The transmitted data may be recorded in analog for another multipoint recorder or may be converted to digital form for recording on punched paper or magnetic tape to be used by a computer or it may be automatically typed on a log sheet. For digital transmission an analog to digital converter sequentially converts the measurement signals to pulsed digital information which is transmitted by telephone to a central station. This data may be recorded on tape for later computer input or may be directly fed into a computer. When storing data on tape for later print-out or computer processing, real time should be recorded from a digital clock to permit complete identification of samples at a later time.

The use of continuous monitoring equipment will permit the frequent measurement of several water quality parameters and will record this data at the measurement site or transmit it to another location. The choice of the best method of data recording and of sensors to be used depends on the purpose of the monitoring. If the monitoring is to provide information on fluctuations in quality which will be used as background data for future studies, telemetering of the data is usually unnecessary. In most studies, however, telemetering of data is important as the scientist may wish to begin sampling for other constituents when one of the continuously measured parameters reaches some high or low value. Water management decisions, such as stopping waste effluent from entering a river or temporary suspension of drawing water from a river, may result from decisions based on these telemetered data. To call attention to values which fall outside the preset level automatic alarms may be added to the system and samples can be collected automatically by a similar circuit actuating an automatic sampling system.

D. Sensors

It would be desireable to have at our disposal a series of sensors, each specific to one physical or chemical parameter of water quality. This level of sophistication has not been achieved, but many analyses can be made continuously or on a sequential basis by automated equipment. The input transducer or sensor responds to a physical or chemical change by a proportional change in a transmittable signal, most commonly an electrical signal. This signal is modified in the measuring system which can be considered as a series of transducers (6); (a) input or measuring transducers, (b) modifying transducers, and (c) output or readout transducers.

Temperature sensors have been recently reviewed by Bollinger (4) who indicates that for continuous monitoring resistance thermometer, thermistors, and thermocouples may be used. Resistance thermometers are based on the temperature dependence of the resistance of most metals. From accurate measurement of the resistance of a coil of metal wire, often nickel or platinum, the temperature can be determined. Thermistors are semiconductors showing a high negative coefficient of resistance as a function of temperature. Changes of resistance by a ratio of 10:1 over the range -100 to +450°C are known. In thermocouples a potential proportional to the difference between the sample and reference temperatures is developed at the junction of two dissimilar metals (Chromel-Alumel for the W-20 sensor).

A number of sensors which are suitable for continuous monitoring of chemical properties are listed in Table VI-1. Many of these have been used in continuous monitoring applications (3). Generally the most serious limitation to the use of many of these sensors is their need to be standardized frequently. This requirement is a serious limitation to their use in remote locations where it may be desireable to service an instrument weekly or semi-weekly. Presently many new specific ion electrodes (Table VI-2) have become commercially available. These electrodes can be adapted easily to use with existing instruments such as the W-20.

Table VI-1. CONTINUOUS SENSORS

Electrical sensors

- Amperometric
- Conductometric (electrical)
- Coulometric
- Galvanic
- Ionization detectors
- Polarographic
- Potentiometric

Optical sensors

- Colorimetric (spectrophotometric, visible region)
- Emission spectroscopic
- Flame photometric
- Fluorimetric
- Infrared spectrophotometric
- Particle counting
- Turbidimetric
- Ultraviolet spectrophotometric

Sensors based on physical properties

- Density
- Optical rotation
- Refractive index
- Viscosity

Sensors based on thermal properties

- Conductivity (thermal)

Sensors based on miscellaneous properties

- Magnetic
- Mass spectroscopy

Sensors based on radioactivity

Table VI-2. COMMERCIALLY AVAILABLE ION-SELECTIVE ELECTRODES

Ion	Membrane	Lower Detection Limit	Principal Interferences
H^+	glass	10^{-14} M	none above pH 13
Na^+	glass	10^{-6} M	H^+, Ag^+
K^+	glass	10^{-6} M	H^+, Ag^+, Na^+
NO_3^-	liquid	10^{-5} M	I^-, Br^-
Cl^-	liquid	10^{-5} M	I^-, NO_3^-, Br^-
Ca^{++}	liquid	10^{-5} M	Zn^{++}, Fe^{++}, Pb^{++}, Cu^{++}
Water hardness	liquid	10^{-8} M	Zn^{++}, Fe^{++}, Pb^{++}, Cu^{++}
F^-	solid	10^{-6} M	OH^- at high pH
Cl^-	solid	5×10^{-5} M	$S^=$, I^-, Br^-, CN^-
Br^-	solid	5×10^{-6} M	I^-, $S^=$, CN^-
I^-	solid	5×10^{-8} M	$S^=$
$S^=$	solid	10^{-17} M	Hg^{++}
CN^-	solid	10^{-6} M	$S^=$, I^-
Ag^+	solid	10^{-17} M	Hg^{++}
Cd^{++}	solid	10^{-7} M	Ag^+, Cu^{++}, Hg^{++}
Pb^{++}	solid	10^{-7} M	Ag^+, Cu^{++}, Hg^{++}
Cu^{++}	solid	10^{-8} M	Ag^+, Hg^{++}

E. Analysis and Control of Biological Processes

As necessary analytical instrumentation becomes available waste treatment plants will be able to substitute these methods rather than using wet chemical methods. These modern methods could be performed on a continuous basis not only to provide instantaneous information on the efficiency of the plant, but also to permit automatic control of the waste treatment facility. This modernization will result in optimization of the treatment process which will insure that the effluent will be of high quality over a wide range of operating conditions. Automation will also reduce the manpower requirements of modern treatment facilities.

Zenz, McAloon, and Weddle (7) have reviewed many of the applicable analyzers which could be used for continuous monitoring for the activated sludge process and anaerobic digestion. Some of the parameters which they considered essential to be monitored continuously included: substrate concentration, suspended solids, toxicants, pH, temperature, dissolved oxygen, nitrogen, phosphorus, conductivity, biological activity, gas composition, and residual chlorine.

A knowledge of the substrate concentration is essential to optimization of treatment. The time lag in the measurement of BOD is too great to permit this determination to be used in controlling plant operations. T he introduction of rapid instrumental methods permits the measurement of substrate concentrations on a time scale required for the obtaining of operating information.

Chemical Oxygen Demand (COD) can be measured using the Technion Autoanalyzer as indicated in the COD experiment. The Precision Aquarator (Precision Scientific Lo.) measures COD in approximately two minutes by carrying the organic matter by dry CO_2 through a platinum catalytic combustion furnace which oxidizes the organic matter to CO and H_2O. Following water removal and passage through a second catalytic treatment, the CO concentration is measured using an infrared analyzer (Figure 1).

In Total Carbon Analyzers (Beckman Instruments, Inc. and Union Carbide Corp.) organic matter is combusted to CO_2, H_2O, and N_2. The CO_2 concentration is determined, subsequent to separation of the H_2O by an infrared analyzer (Figure 2). The analysis will determine the total carbon content of the sample unless the carbonate is removed by acidification and nitrogen purging of the sample prior to analysis. If this is done the sample can be analyzed for total organic carbon (TOC).

Another analyzer (Rocket dyne) employs pyrolytic fragmentation of the organics in the presence of water. The fragments are then measured with a hydrogen flame ionization detector. This analyzer does not respond to inorganic carbonates or dissolved carbon dioxide in the sample.

Suspended solids can be continuously measured by the absorption or reflection of energy. Presently visible light, infrared radiation, ultrasonic waves and gamma radiation are used for solids determinations. Of these visible light has been used the most. Because of its limited penetrating power, its absorption or reflection

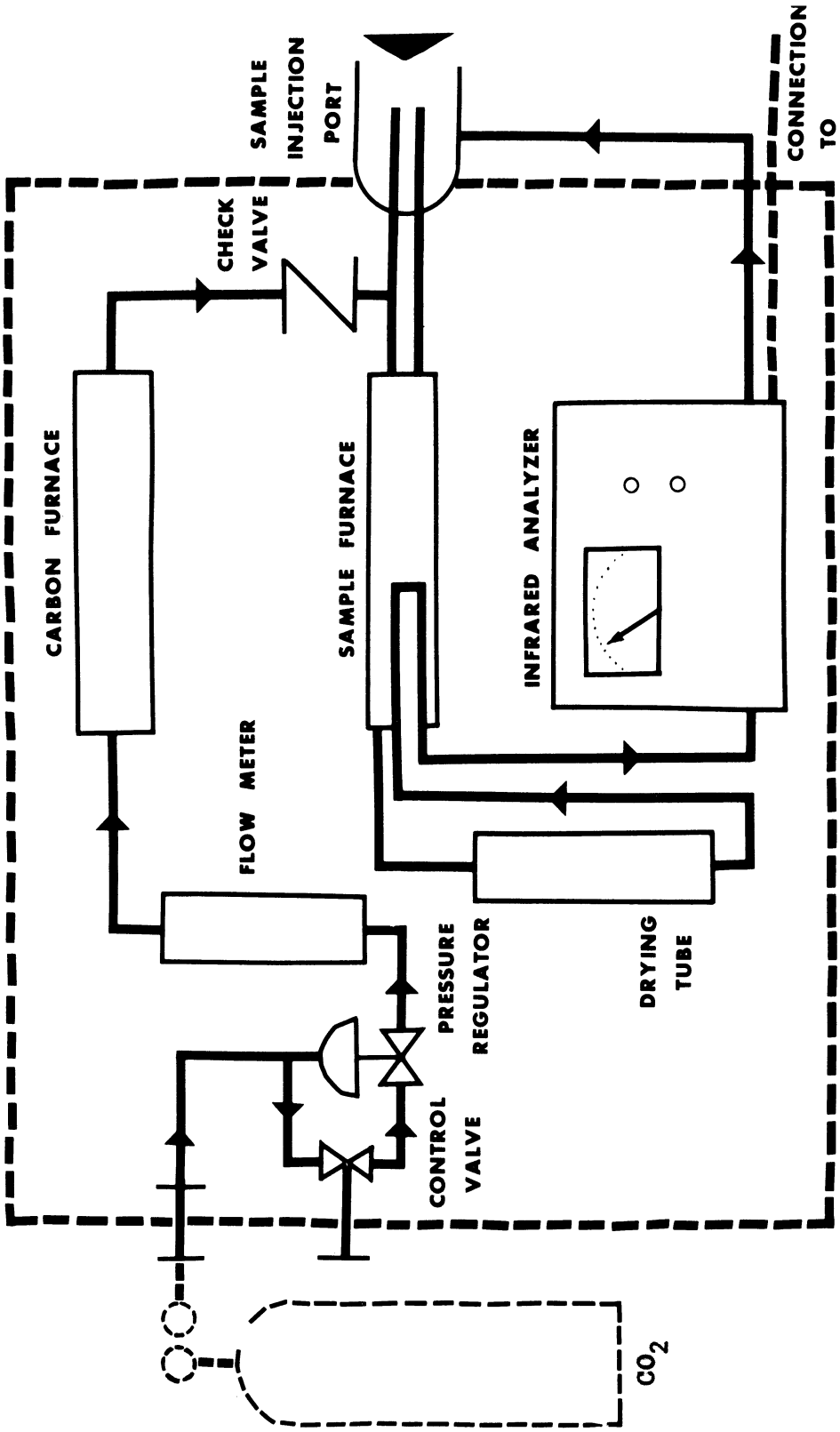


Figure VI-1. COD Analyzer Flow Diagram

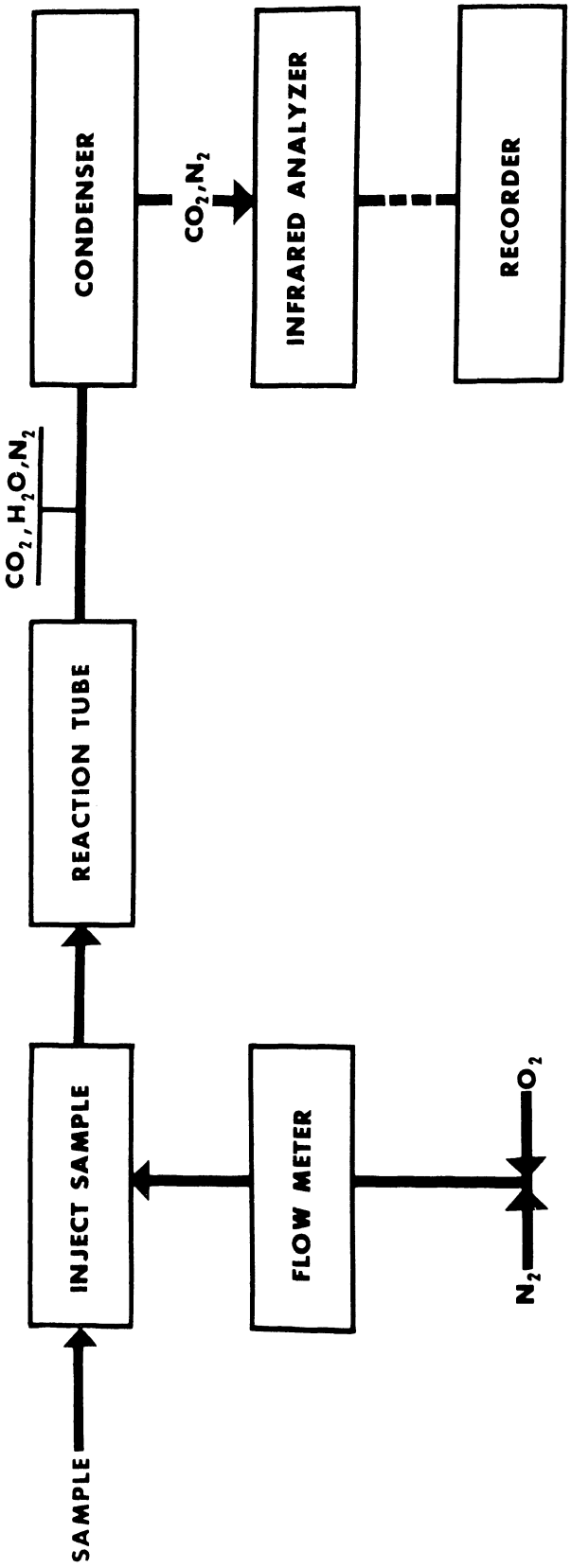


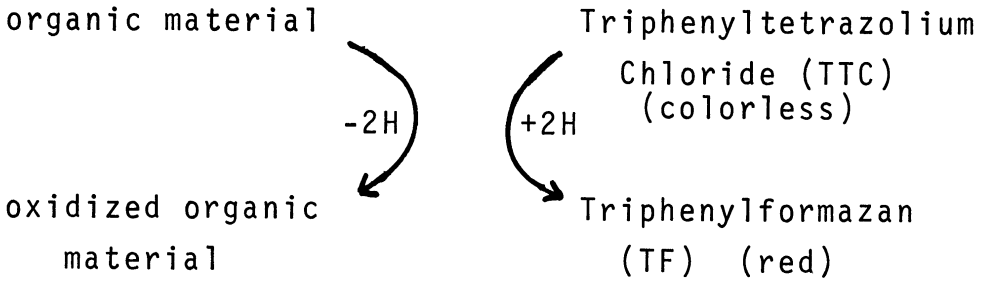
Figure 2. Total Carbon Analyzer Flow Diagram

depends mainly on the surface area of the solids rather than their volume and density. These instruments require low flows to prevent light losses at the liquid surface. In wastewaters of high suspended solids, clogging may occur.

Analyzers employing infrared radiation measure dissolved solids concentrations more satisfactorily than visible light instruments due to the greater penetrating power of infrared radiation. Ultrasonic radiation do not appear to be sufficiently sensitive to measure suspended solids concentrations of less than one percent. The equipment required can be as much as ten times as expensive as visible or infrared measuring devices.

Gamma radiation devices using cesium-137 or other isotopes lacking strong beta radiation have great penetrating power. This equipment is applicable to monitoring large process lines for the solids concentrations found in the activated sludge process. The equipment required is expensive, and requires special maintenance, calibration and supervision.

The biological activity in the activated sludge process has not been satisfactorily monitored on a continuous basis, but several new methods appear to be applicable to the new problem. The activity of the dehydrogenase enzyme can be monitored continuously by a colorimetric analytical procedure and can be used to control the process. The reaction associated with the measurements is as follows:



(VI-1)

The TF is insoluble in water, but soluble in alcohol.

Biological activity could also be monitored by measuring the rate of oxygen uptake. Samples can be withdrawn automatically and their oxygen concentration monitored for a given time using a dissolved oxygen probe.

The active mass of bacteria may be measured, not only in waste reactors but also in natural water systems, by monitoring the amount of adenosine triphosphate (ATP). This procedure involves the addition of the sample to a buffered reaction mixture of luciferin and luciferase (materials obtained from firefly tails) and measuring the light produced.

Two basic types of instruments are available for the measurement of conductance. The more familiar system imposes an AC potential between a pair of platinum electrodes and measures their resistance which is a function of the conductance of the solution. Electrodeless conductivity systems eliminate the problem of coating of the electrodes. The system measures changes in inductance or capacitance

due to the sample which is not in physical contact with the cell. The inductance of capacitance can then be related to the sample's conductance.

Residual chlorine can be monitored by amperometric instrumentation. The sample passes a pair of electrodes of dissimilar metals. The polarization of the nobler 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. Since a continuous signal is obtained from this type of instrument, it is possible to automatically control the addition of chlorine to the system.

The gas composition and volatile acids content of anaerobic digestors can be monitored by gas chromatography. The automation or gas chromatography has been achieved for some industrial applications, but this has not yet been extended to the waste treatment field. Further research and development will be required before gas chromatography can be used to continuously monitor and control the anaerobic digestion process.

Many of the other instrumental methods required for the monitoring of waste treatment facilities have been discussed elsewhere in this book. Nitrogen, phosphorus and specific toxicants can be measured by the Auto Analyzer while heavy metals can be analyzed by atomic spectroscopy or with specific ion electrodes for some metals. Electrode systems are also used for the measurement of dissolved oxygen and pH while temperature can be measured by thermistors or thermocouples.

F. Noncontact Methods

Aerial photography has been extremely beneficial in mapping hydrologic features and has been used to a limited extent in pollution surveys. Infrared mapping of natural waters has been used only in a few instances, but is an extremely useful tool in the study of heated discharges.

All objects whose temperatures are above absolute zero emit electromagnetic radiation. Although this energy is emitted over a wide band of wavelengths, natural waters will emit a maximum amount of radiant energy in the infrared. The maximum energy emission shifts to shorter wavelengths with increasing temperature. Any object which is a perfect absorber and emitter of radiant energy is called a "blackbody" and, by definition, has an emissivity value of 1. Natural water has an emissivity between 0.95 and 0.993 (5). The total radiated energy from a body is expressed by the Stefan-Boltzmann law

$$W = \varepsilon\sigma T^4 \qquad \text{(VI-2)}$$

where W is the total radiant emittance, Watts/cm^2, ε is the emissivity value, T is the temperature, degrees Kelvin, and σ is the Stefan-Boltzmann constant, 5.673×10^{-12} Watts/cm^{2}deg^4.

Infrared radiometers usually measure the energy emitted in the 8 to 14μ portion of the spectrum. This region includes the peak emission wavelength of natural water and atmospheric components such as water vapor, carbon dioxide, and ozone do not absorb this radiation. The use of such radiometers mounted in airplanes permits rapid surveys of current patterns and mixing of industrial waste effluents in rivers and lakes. The instrument sequentially scans fields at the same time the aircraft is moving. During the flight a map of 8 to 14μ radiation intensities is produced by conversion of differences in the radiation intensity to a signal which can be recorded on photographic film as shades of gray. Since waste effluents are generally of a different temperature than the receiving stream, this technique can easily survey the location of all effluents entering a stream.

REFERENCES

1) F. A. J. Armstrong and E. C. LaFond, Limnol. and Oceanogr., 11, 538 (1966).

2) M. Bernhard and G. Macchi, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 255.

3) W. J. Blaedel and R. H. Laessig, "Advances in Analytical Chemistry and Instrumentation," Vol. 5, C. N. Reilley and F. W. McLafferty, Eds., Interscience Publishers, New York, N.Y., 1966, p. 69.

4) L. Bollinger, "Environmental Measurements: Valid Data and Logical Interpretation," U. S. Public Health Service Publ. No. 999-WP-15, Washington, D.C., 1964, p. 41.

5) J. R. Van Lopik, G. S. Ramble, and A. E. Pressman, J. Water Poll. Contr. Fed., 40, 425 (1968).

6) P. K. Stein, "Environmental Measurements: Valid Data and Logical Interpretation," U. S. Public Health Service Publ. No. 999-WP-15, Washington, D.C., 1964, p. 65.

7) D. R. Zenz, T. J. McAloon, and C. L. Weddle, "Sensors for the Analysis and Control of Biological Processes," presented to the Division of Water, Air, and Waste Chemistry, American Chemical Society, Minneapolis, Minnesota, April 17, 1969.

VII. AUTOMATED CHEMICAL ANALYSES

The water analyst is presently faced with a rapidly increasing number of requests for routine analyses of water samples. To facilitate the analysis of large numbers of samples the chemist has begun using automated methods of analysis. It is the purpose of this chapter to describe the Technicon AutoAnalyzer, an instrument for automated colorimetric chemical analyses, and to detail important points in its operation.

Automation of wet chemical methods not only permits the analysis of larger numbers of samples than can be analyzed manually, but also offers higher precision than manual methods. Human errors are minimized by the automatic proportioning of sample and reagent and development and measurement of the color produced. Since the entire procedure including reagent addition, mixing and heating are exactly reproduced, methods which might be difficult or impossible manually can be used on the AutoAnalyzer. However, when an automated procedure is adopted, the chemist loses much of the control over specific steps that he had with manual methods. Due to the time required to prepare the AutoAnalyzer for an analysis, it is not advantageous to run less than twenty tests except for the most difficult manual procedures.

A. System Design

The Autoanalyzer is an instrument capable of automatic sampling, filtering, diluting, reagent addition, mixing, heating, digesting, and after appropriate delay for color development, measurement of the color produced. All operations are performed on a stream which is moved by a fixed speed peristaltic pump. This pump together with the manifold that fits onto it forms the heart of the AutoAnalyzer system. The pump can accomodate as many as fifteen tubes, the inside diameters of which are proportional to the flow rate (Table VII-1). Diffusion or cross-contamination of samples is prevented by the segmentation of the sample stream by air bubbles. The sample, air and various reagent streams are brought together

Table VII-1. TUBE SIZES AND DELIVERIES WITH STANDARD AUTOANALYZER PUMP

Tube		Clear Standard Delivery cc/min			Solvaflex Delivery cc/min			Acidflex Delivery cc/min (approx)
I.D.	Shoulder Colors	Min.	Nom.	Max.	Min.	Nom.	Max.	
.005	Orange Black	.005	.015	.029	.005	.015	.029	n.a.*
.0075	Orange Red	.016	.03	.048	.016	.03	.048	n.a.
.010	Orange Blue	.032	.05	.072	.032	.05	.072	n.a.
.015	Orange Green	.075	.10	.128	.075	.10	.128	n.a.
.020	Orange Yellow	.13	.16	.19	.13	.16	.19	n.a.
.025	Orange White	.19	.23	.27	.19	.23	.27	n.a.
.030	Black	.28	.32	.36	.28	.32	.36	0.34
.035	Orange	.37	.42	.47	.37	.42	.47	0.43
.040	White	.54	.60	.66	.51	.56	.62	0.53
.045	Red	.73	.80	.87	.64	.70	.76	0.64
.051	Grey	0.92	1.00	1.03	0.81	0.88	0.93	0.78
.056	Yellow	1.12	1.20	1.28	.99	1.06	1.13	0.92
.060	Yellow-Blue	1.31	1.40	1.49	1.14	1.21	1.29	1.06
.065	Blue	1.50	1.60	1.70	1.29	1.37	1.45	1.19
.073	Green	1.90	2.00	2.10	1.60	1.69	1.78	1.44
.081	Purple	2.37	2.50	2.63	1.92	2.02	2.12	1.71
.090	Purple Black	2.77	2.90	3.03	2.31	2.42	2.53	2.03
.100	Purple Orange	3.26	3.40	3.54	2.77	2.89	3.01	2.39
.110	Purple White	3.75	3.90	4.05	3.26	3.39	3.52	2.76
.110	Purple White	3.75	3.90	4.05	3.26	3.39	3.52	2.76

* n.a. = not available

by the use of 'h', 'T', or other shaped glass fittings. Mixing of the stream containing the sample plus reagents is accomplished in a vertical mixing coil which causes the stream to be inverted a number of times.

Samples are supplied from the sampler which contains a removable circular turntable which can accomodate forty sample cups. Between samples the probe aspirates a wash solution whose receptical is kept filled by the pump. A cam determines the aspiration time of the sample and wash solution. The ratio of sample to wash time is usually 2:1 and twenty to sixty tests/hour are performed although cams are available for 10 to 120 tests/hour with eleven different sample-to-wash ratios of 6:1 to 1:6.

Time delay coils and heating baths are used to permit sufficient time and heat for reactions to take place. The coils are horizontal and therefore provide no mixing. Coils 10, 20, and 40 feet long are available. Heating baths used for water analyses usually are provided with adjustable thermoregulators with maximum temperatures of 100° or 200°C. The higher temperature is needed for the determination of chemical oxygen demand and in procedures employing a distillation (e.g. phenol and fluoride).

The continuous digestor module has been used primarily for the automation of Kjeldahl nitrogen analyses, but has also found use in the digestion of organic phosphates (7) and for the analysis of chemical oxygen demand (70). The digestor is capable of operating at temperatures as high as 700°C; for any procedure the digestor may be operated at a sufficiently high temperature to insure rapid and complete destruction of organic matter. Sample and digestion fluid are pumped into the glass digestor tube which is helically grooved and is slowly rotated by a motor, causing the sample to be spirally transported to the other end. Two independently controlled are used in the digestor; the first stage heater causes the water to be vaporized and begins the oxidation of the sample. The second stage heater, which is maintained at a higher temperature than the first, completes the oxidation of the sample. At the exit end of the helix, water is added and the diluted material is aspirated into a small mixing chamber before passing to the manifold where the chromogenic reagents will be added to the sample.

Turbidity in samples may be removed by the use of the continuous filter or dialysis modules. Although either method may be used only 10 to 15 percent dialysis is generally achieved since sufficient time is not permitted to approach the 50 percent maximum. Unless samples contain high levels of the constituent to be analyzed, dialysis will not be useful to the analyst. Filtration, either manual or by use of the Technicon continuous filter, is the usual procedure prior to analysis of water samples.

The color measurement is performed in a filter photometer equipped with a flow-cell. Prior to the sample stream entering the colorimeter, air bubbles are removed. The debubbling is achieved by pulling only a portion of the liquid stream through the colorimeter cell by a tube in the pump. Air bubbles and the remaining portion of the liquid stream are discharged to a waste line. Figure VII-1 shows the details of the flow cell and debubbler assembly. Various length flow cells can be accommodated in the colorimeter but for water analyses a 50 mm cell is generally used to gain sensitivity. Range expanders are often required to improve the readability of the recorder chart. The range expander allows full scale recorder deflection to represent 50-100% (2x), 75-100% (4x), or 90-100% (10x). With the adjustable model range expander any 50%, 25%, or 10% range may be magnified to full scale deflection. For many tests on natural water the analyst deals with concentrations near the limit of sensitivity of available analytical procedures and must use both long cells and a range expander.

The percent transmission of the samples is recorded on the recorder chart. For those tests obeying the Beer-Lambert law, the percent transmission of the standards can be plotted on semi-logarithmic paper if no range expansion was used. If 4x or 10x range expansion was used, the recorder response should be plotted on linear paper since in the ranges of 75 to 100 and 90 to 100 the logarithm of a number and the number are approximately proportional. When 2x range expansion is used, the plot will generally be most nearly linear if made on semi-logarithmic paper. For the most precise work in all cases, absorbances should be calculated and plotted bs. the concentration. Table VII-2 is a listing of a Fortran IV program which computes absorbances of samples from the recorder response. The slope and intercept of the standard series is computed by the method

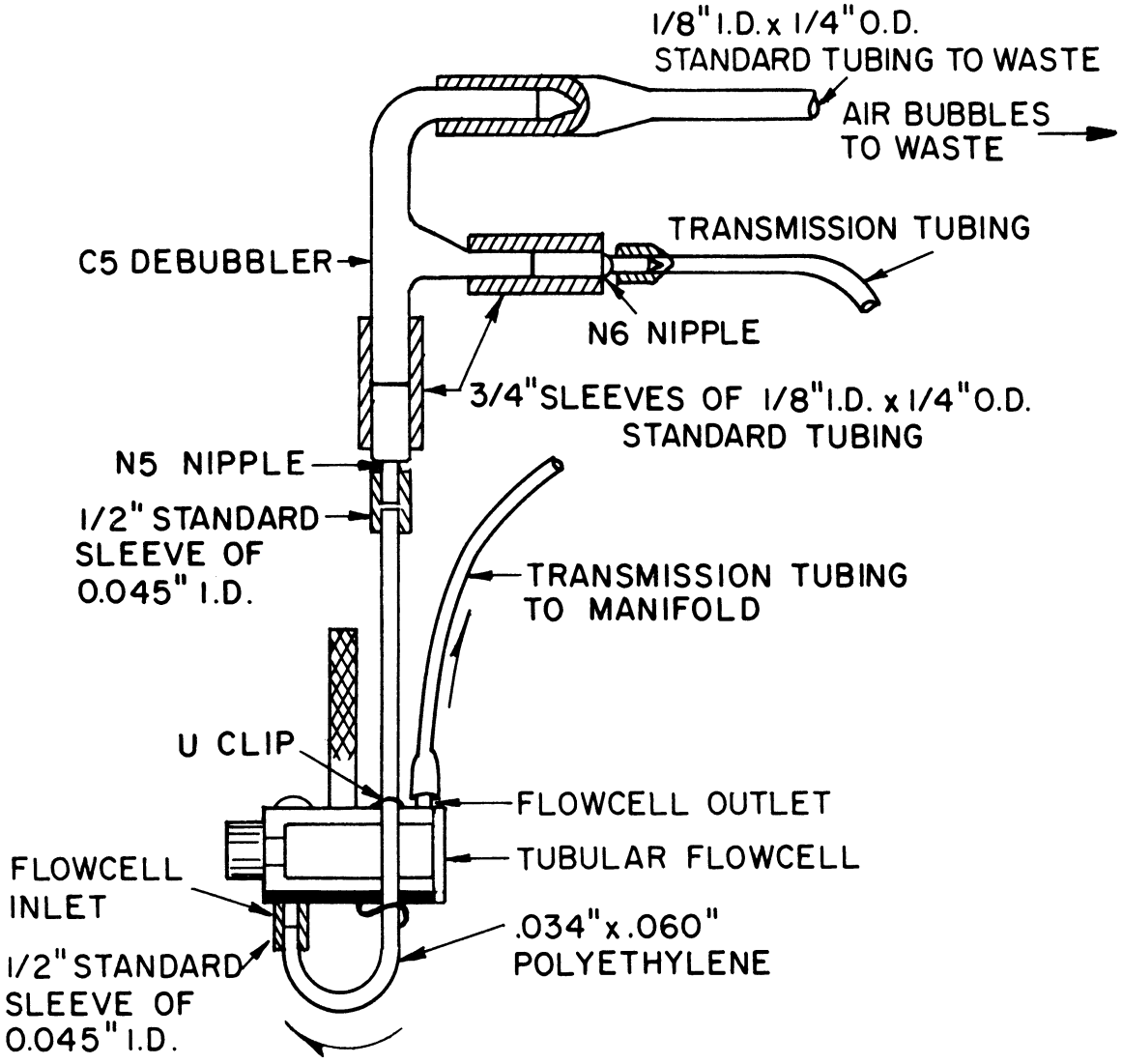


Figure VII-1. AutoAnalyzer Flowcell Tubing Connections

Table VII-2. Computer Program (Fortran IV) for the Analyses of AutoAnalyzer Data

```
C........ LIST OF VARIABLES........
C...
C...A                    SUM OF ABSORBANCES
C...C                    SUM OF CONCENTRATIONS
C...AA                   SUM OF (ABSORBANCES)**2
C...CC                   SUM OF (CONCENTRATIONS)**2
C...AC                   SUM OF (ABSORBANCE)*(CONCENTRATION)
C...CONST                CONVERSION CONSTANT
C...NSTD                 NUMBER OF STANDARDS
C...NSAMP                NUMBER OF SAMPLES
C...RANGE,IRANG          RANGE EXPANSION
C...TBASB                BASE LINE TRANSMITTANCE BEFORE SET
C...TBASA                BASE LINE TRANSMITTANCE AFTER SET
C...MO                   MONTH
C...DAY                  DAY
C...COMM                 COMMENT FIELD
C...ABASB                BASE LINE ABSORBANCE BEFORE SET
C...ABASA                BASE LINE ABSORBANCE BEFORE SET
C...DBASE                DIFFERENCE IN BASE LINE BEFORE AND AFTER (DRIFT)
C...CONC                 CONCENTRATION OF STANDARDS
C...TRANS                TRANSMITTANCE OF PERCENT TRANSMISSION*100.
C...COM                  COMMENT FIELD
C...ABSM                 MEASURED ABSORBANCE
C...ABS                  TRUE ABSORBANCE
C...SLOPE                SLOPE OF CONCENTRATION VS. ABSORBANCE
C...INCPT                INTERCEPT OF ABSORBANCE AXIS
C...CORCO                CORRELATION COEFFICIENT
C...NUM                  NUMBER OF STANDARDS + SAMPLES + 1
C...IBOT                 SAMPLE IDENTIFICATION (BOTTLE NUMBER)
C...
      INTEGER DAY
      REAL INCPT
      DIMENSION COMM(14),COM(7)
      CONST=0.4342945
C........INITIALIZATION OF VALUES USED FOR LEAST SQUARES ANALYSIS
   10 A=0.
      C=0.
      CC=0.
      AA=0.
      AC=0.
C........INPUT FOR SET CONTROL CARD
C........VARIABLE.....................INPUT COLUMNS....FIELD TYPE....EXAMPLE..
C...
C...NSTD    (NUMBER OF STANDARDS)          1-3            I3          006
C...NSAMP   (NUMBER OF SAMPLES)            4-6            I3          012

C...RANGE   (RANGE EXPANSION)              7-8           F2.0           01
C...TBASB   (BASE LINE PERCENT TRANSMISSION 9-12          F4.3         1000
C...TBASA     *100. BEFORE AND AFTER SET)  13-16          F4.3         0975
C...MO      (MONTH)                       17-18           I2           02
C...DAY     (DAY)                         19-20           I2           14
C...COMM    (COMMENT FIELD)               21-76         14A4       **TITLE**
C...
      READ(2,20)NSTD,NSAMP,RANGE,TBASB,TBASA,MO,DAY,COMM
   20 FORMAT(2I3,F2.0,2F4.3,2I2,14A4)
      IF(NSTD) 100,100,27
C........BASE LINE DRIFT COMPUTED (DBASE)
   27 ABASB=CONST*FALOG(1./(1.-(1.-TBASB)/RANGE))
      ABASA=CONST*FALOG(1./(1.-(1.-TBASA)/RANGE))
      DBASE=ABASA-ABASB
```

Table VII-2. Computer Program (Fortran IV) for the Analyses of AutoAnalyzer Data (cont.)

```
C........HEADING FOR OUTPUT OF STANDARDS
      WRITE(3,11)MO,DAY
   11 FORMAT(1H1,50X,I2,'/',I2)
      WRITE(3,14)COMM
   14 FORMAT(1H0,30X,15A4// 50X,'STANDARDS'/)
      WRITE(3,15)
   15 FORMAT(1H ,T32,'MEASURED',T47,'MEASURED',T63,'TRUE'/ T30,'TRANSMIS
     1SION ',T46,'ABSORBANCE',T60,'ABSORBANCE',T75,'CONCENTRATION'/)
C........INPUT FOR STANDARDS
C........VARIABLE.....................INPUT COLUMNS....FIELD TYPE....EXAMPLE..
C...
C...CONC   (CONCENTRATION OF STANDARD)      1-6          F6.2         025000
C...TRANS  (PERCENT TRANSMI&SION * 100.)    7-10         F4.3          0750
C...COM    (COMMENT FIELD)                 11-38         7A4        **REMARKS*
C...
      DO 40 I=1,NSTD
      READ(2,50)CONC,TRANS,COM
   50 FORMAT(F6.2,F4.3,7A4)
C........COMPUTE MEASURED AND  TRUE ABSORBANCE
      ABSM=CONST*FALOG(1./(1.-(1.-TRANS)/RANGE))
      NUM=NSTD+NSAMP+1
      ABS=ABSM-ABASB-(I*DBASE/NUM)
C........OUTPUT FOR STANDARDS
      WRITE(3,60)TRANS,ABSM,ABS,CONC,COM
   60 FORMAT(1H ,T33,F6.4,T47,F7.4,T61,F7.4,T78,F8.3,T89,7A4)
C........COLLECT DATA FOR LEAST SQUARES ANALYSIS
      A=A+ABS
      AA=AA+ABS*ABS
      C=C+CONC
      CC=CC+CONC*CONC
   40 AC=AC+ABS*CONC
C........COMPLETE THE LEAST SQUARES ANALYSIS AFTER INPUT OF ALL STANDARDS
      SLOPE=(NSTD*AC-A*C)/(NSTD*CC-C*C)
      INCPT=A/NSTD-SLOPE*C/NSTD
      CORCO=(NSTD*AC-C*A)/SQRT((NSTD*CC-C*C)*(NSTD*AA-A*A))
      IRANG=RANGE
      WRITE(3,70)SLOPE,INCPT,CORCO,IRANG,ABASB,ABASA
   70 FORMAT(1H0,5X,110('*')/ 10X,'SLOPE = ',E12.4,10X,'INTERCEPT = ',
     1F7.4/10X,'CORRELATION COEFFICIENT = ',F6.4,10X,'RANGE EXPANSION '
     2I2,'X'/10X,'THE BASE LINE SHIFTED FROM AN ABSORBANCE OF ',F6.3,'T
     30',F6.3/5X,110('*')/)
C........IF THERE ARE NO SAMPLES, RETURN TO INITIALIZE FOR A NEW SET
      IF(NSAMP)10,10,80
   80 WRITE(3,85)
   85 FORMAT(1H ,50X,'SAMPLES'/T10,'BOTTLE',T32,'MEASURED',
     1T47,'MEASURED',T63,'TRUE'/ T10,'NUMBER',T30,'TRANSMISSION',T46,
     2'ABSORBANCE',T60,'ABSORBANCE',T75,'CONCENTRATION'/)
C........INPUT FOR SAMPLES
C........VARIABLE.....................INPUT COLUMNS....FIELD TYPE....EXAMPLE..
C...
C...IBOT   (SAMPLE IDENTIFIER)              1-6           I6          000015
C...TRANS  (PERCENT TRANSMISSION * 100.)    7-10        F4.3           0876
C...COM    (COMMENT FIELD)                 11-38         7A4        **REMARKS*
C...
      DO 90 I=1,NSAMP
      READ(2,86)IBOT,TRANS,COM
   86 FORMAT(2X,I4,F4.3,7A4)
C........COMPUTE MEASURED AND TRUE ABSORBANCE, AND CONCENTRATION FOR SAMPLES
      ABSM=CONST*FALOG(1./(1.-(1.-TRANS)/RANGE))
      ABS=ABSM-ABASB-((I+NSTD)*DBASE/NUM)
      CONC=(ABS-INCPT)/SLOPE
C........OUTPUT FOR SAMPLES
   90 WRITE(3,95)IBOT,TRANS,ABSM,ABS,CONC,COM
   95 FORMAT(1H ,T12,I4,T33,F6.4,T47,F7.4,T61,F7.4,T78,
     1F8.3,T89,7A4)
      GO TO 10
  100 CALL EXIT
      END
```

of least squares and this data is used to compute the absorbance of the samples. Drift of the base-line is assumed to be linear and is compensated. Instruction for the data input is contained within the program in the form of comments.

B. Response Characteristics of Flow Systems

Typical recordings for the analysis of chloride are shown in Figure VII-2. The delay time (t_d) between the beginning of sampling and a response on the recorder is independent of the sampling rate. This is the time required for reagent addition and mixing prior to the sample entering the flow cell. The delay time is dependent on the length of coils and other components in the system and on the flow rate of fluids. The delay for many systems is 5-20 minutes. The total time required for a series of analyses is the delay time plus the product of the number of samples and the sampling rate.

Movement of the sample probe from the wash receptical to a sample causes a step change in concentration which is maintained to the flow cell because of the prevention of diffusion by air bubbles. The change in recorder response when a sample enters the flow cell is not a step change (Figure VII-3). The transition time (t_t) or time for the system to reach a new steady state absorbance is due primarily to mixing in the flow cell (9). This time will be longer with long flow cells than with short ones. The response time, of course, is also governed by the rate at which the sample is pulled through the colorimeter cell. The response curves for two different diameter pull through tubes are shown in Figure VII-3. To obtain optimal response this tube should provide a high flow rate. The maximum size of the pull through tube is governed by the flow rate of the liquid entering the debubbler. To insure air bubbles not entering the flow cell a portion of the liquid must be passed into the waste line at this point and the maximum flow in the flow cell pull through tube must therefore be somewhat less than the total liquid flow. If an analysis has a 0.051" sample tube, 0.040" air tube, and reagent tubes 0.035, 0.040, and 0.051", the total fluid flow is 3.62 ml/min of which 3.02 ml/min is liquid and 0.60 ml/min is air. The maximum size of the flow cell

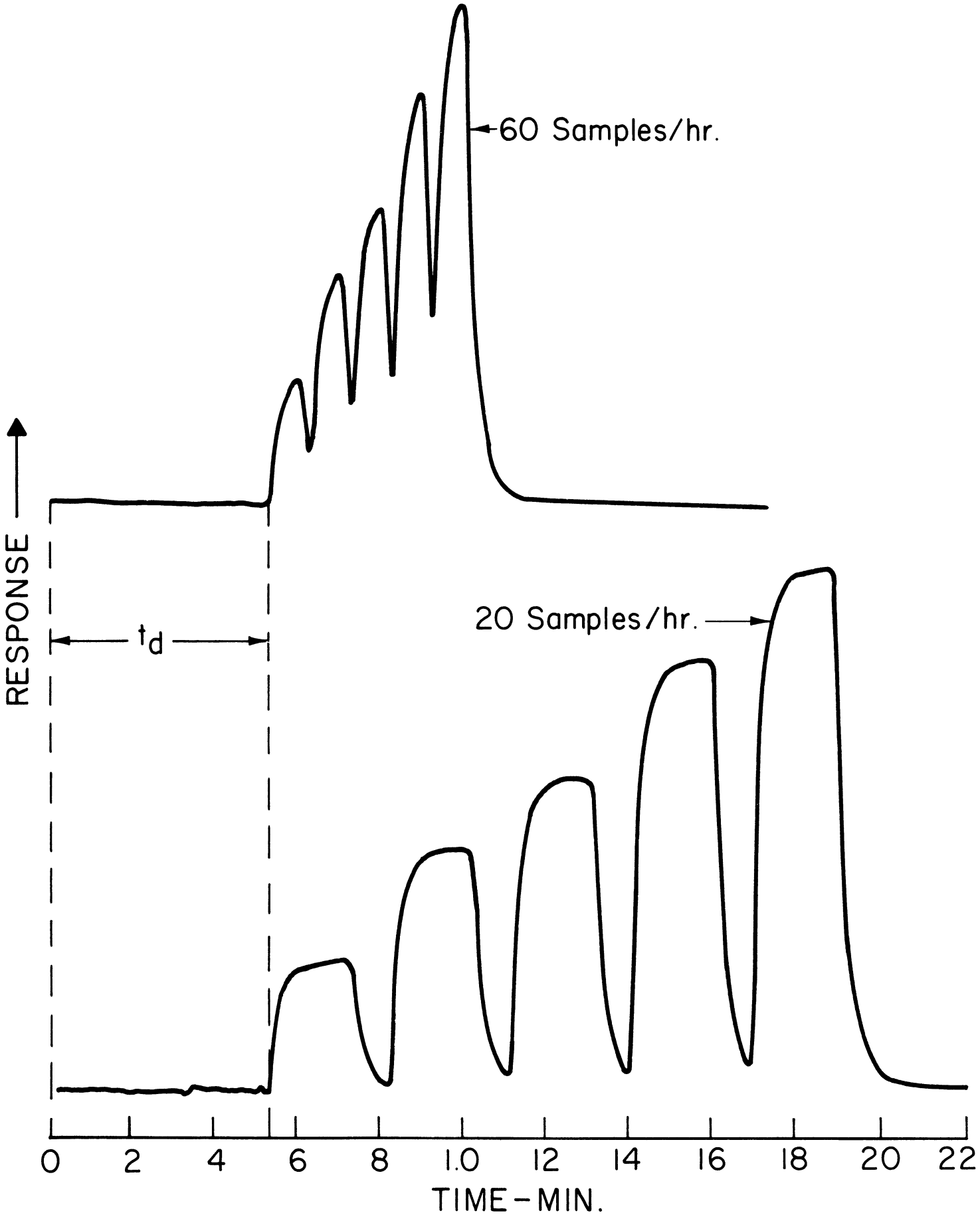


Figure VII-2. Standard series run at 20 and 60 samples/hour. The delay (t_d) is independent of sampling rate.

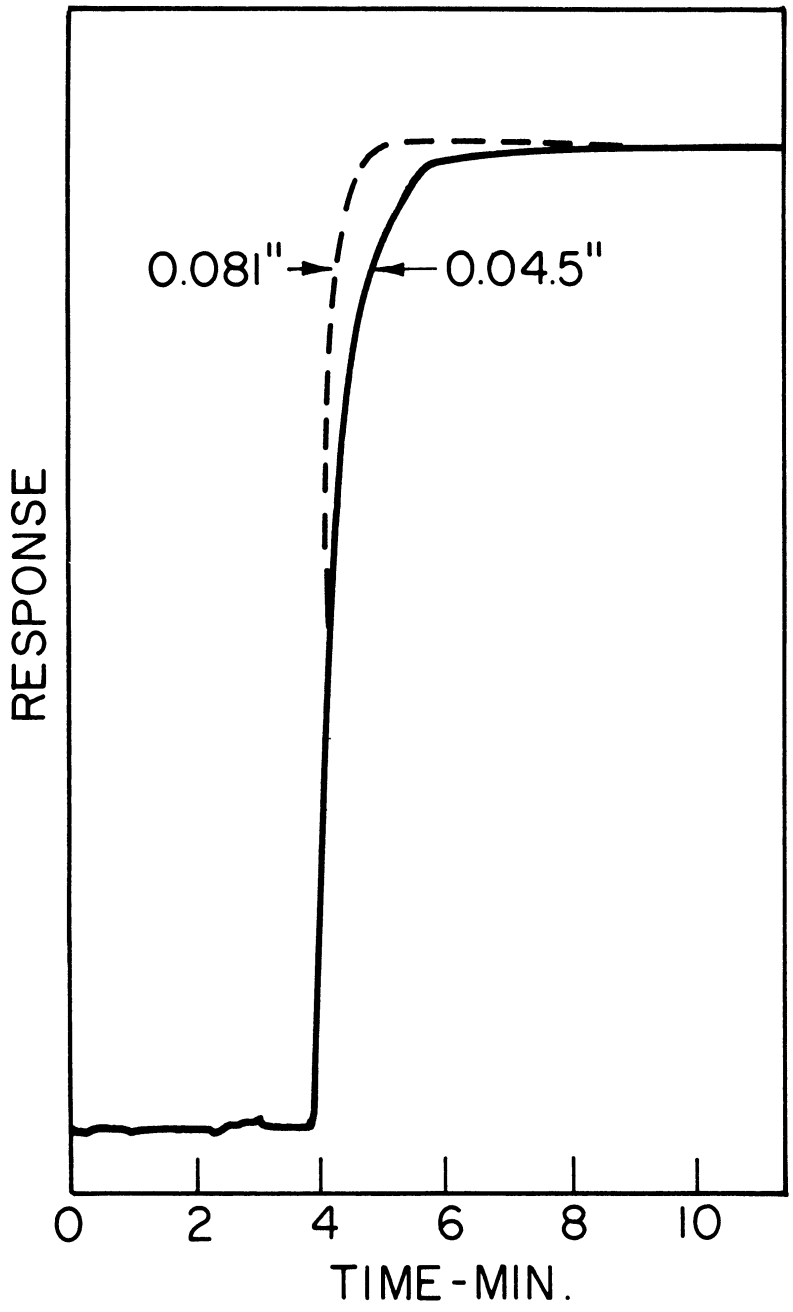


Figure VII-3. Response of the AutoAnalyzer to a step change in concentration using 0.081 and 0.045 inch tubing to pull the sample through the flowcell.

pull through tube should be 0.081" (2.50 ml/min) rather than 0.90" (2.90 ml/min) since the latter might permit occasional air bubbles to enter the flow cell causing erratic readings. The effect of a small air bubble in the flow cell is shown in Figure VII-4. The transient response has been shown to follow first order kinetics (67).

The maximum sampling rate is governed by the length of the flow cell and the rate at which liquid is pulled through it. Figure VII-5 shows the response of a system with a 50 mm flow cell to three samples using different sampling rates. Samples A and C are the same concentration while sample B is approximately six times the concentration. At the slower sampling rate the response to samples A and C is identical but at the higher rate the response to sample C is significantly higher than to sample A. This is due to insufficient time to flush sample B from the cell by the wash solution and sample C. The interaction between samples B and C

$$\text{interaction} = \frac{c-a}{b} \qquad \text{(VII-1)}$$

where a, b, and c are the apparent concentrations of samples A, B, and C

has been shown to be independent of the concentration of the samples used (68). The analyst may therefore correct for the influence of one sample upon the next. Using 50 mm flow cells the response will usually approach the steady-state value, but with shorter cells one may use high sampling rates and not achieve a steady state response. This is possible with the AutoAnalyzer due to the high degree of reproducibility in the processing of samples.

The recorder chart is valuable to the analyst for checking the performance of the instrument and to evaluate the precision obtainable in an analytical procedure. A simple test which should be run for each procedure is the recording of the steady-state response. The sample probe should be placed in a beaker containing a mid-range standard or a typical sample and this solution should be pumped through the system for at least ten minutes. Inspection of the chart will indicate the noise level from both instrumental and chemical factors.

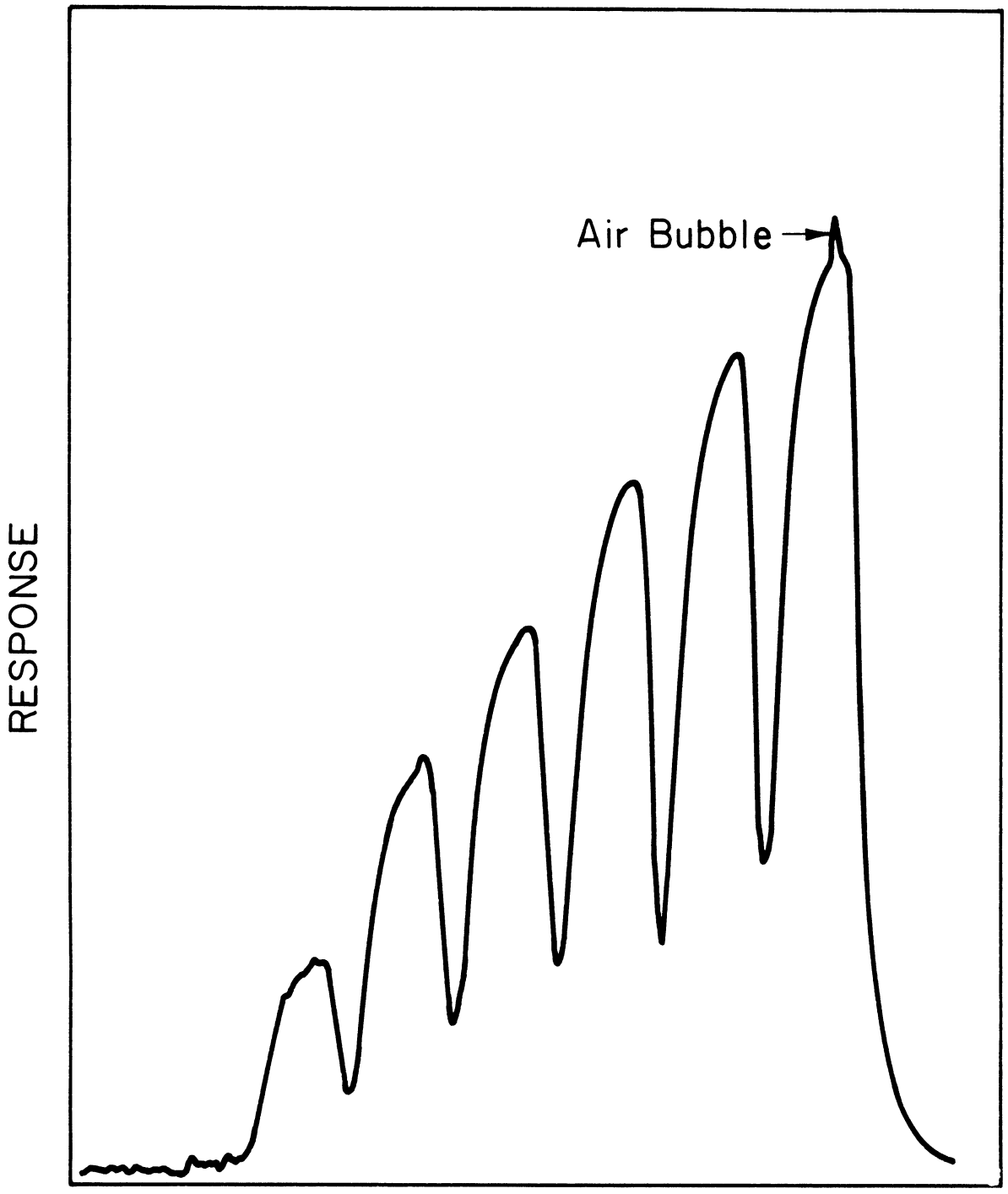


Figure VII-4. Effect of an air bubble in the flowcell on the recorder response.

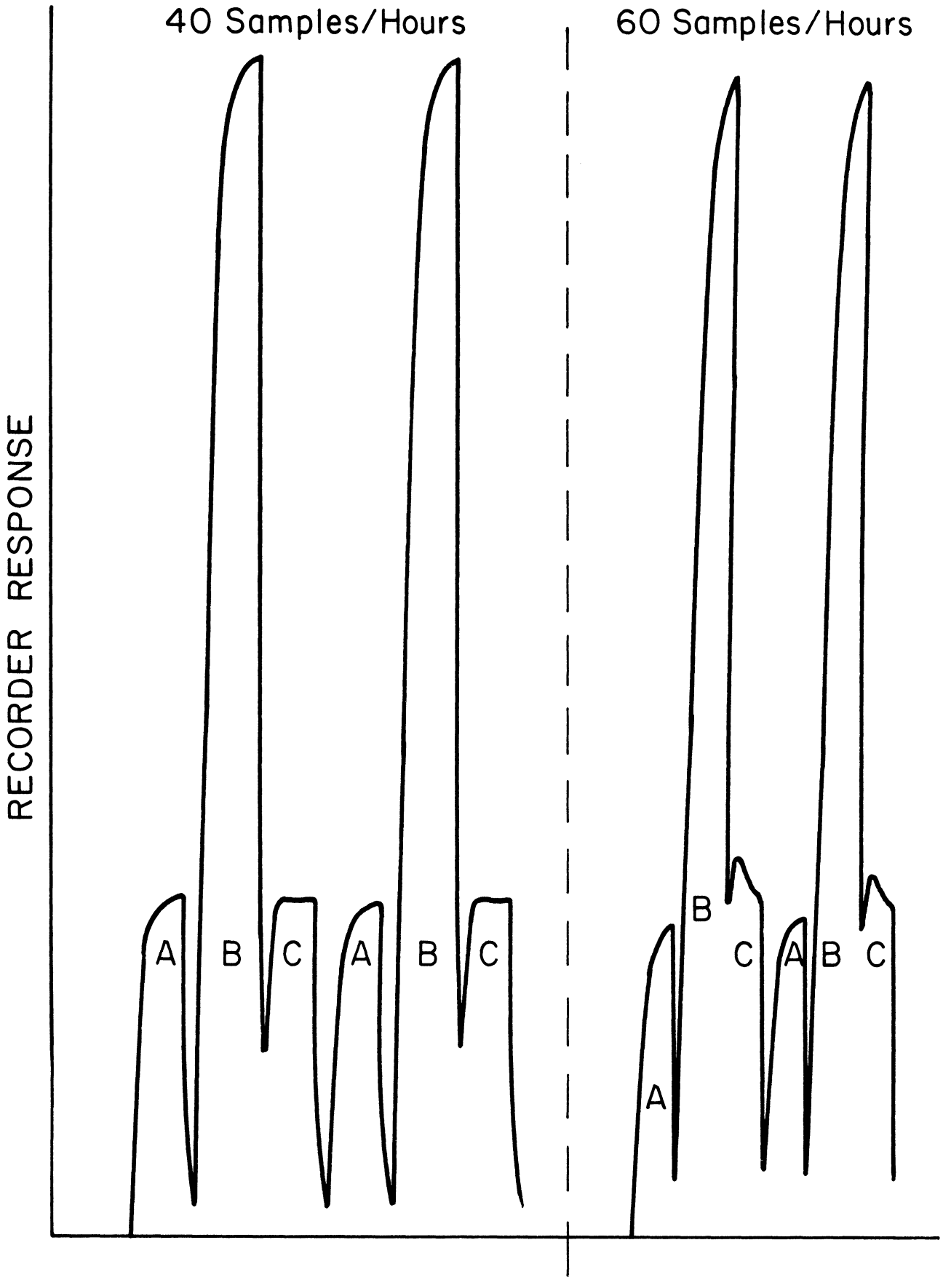


Figure VII-5. Interaction of samples at high sampling rates.

C. Automation of Manual Procedures

Although most methods for automated analysis are based on manual procedures, important changes must usually be made before methods can be successfully automated. When the analyst compares a manual and the corresponding automated method he will usually find that the ratio of sample to reagents is much greater for the manual than the automated procedure. As has been noted it is desirable to maintain a high flow in the system to obtain optimum response. It is difficult hydrodynamically to join streams of high and low flows and with small diameter pump tubes it will frequently be difficult to begin liquid flow when starting the pump. Reagents used in automated methods are often more dilute than for the corresponding manual procedure and in some cases the composition will be changed so the pH will be correctly maintained.

The time and temperature conditions specified in a manual method may be changed in an automated method. In many manual procedures fifteen minutes often passes between the addition of one reagent and the next while in automated methods this is rarely the case. In manual procedures, especially when the chemist must analyze many samples it is difficult, if not impossible, to reproduce exactly the time at which various reagents are added. For this reason, reactions are allowed to go to completion in most manual methods. The excellent reproducibility of the AutoAnalyzer eliminates the need for allowing reactions to achieve completion. Some extremely slow reactions, which take hours of reaction time in manual procedures, can be run at higher temperatures in automated procedures. For methods determining classes of compounds or chemical properties of systems (e.g. total phosphorus, phenols, or COD), different compounds will react with different velocities. When using such a method results more precise but different from manual methods may result. The analyst should verify that comparable results are obtained for both procedures.

If samples contain higher concentrations than can be determined by a given method, the analyst must dilute the sample. If only infrequent samples contain high concentrations, manual dilution should be used. If all samples to be analyzed are too concentrated the

sensitivity of the method should be decreased by using a smaller diameter pump tube for the sample and including another tube to pump a compensating volume of distilled water. Another dilution procedure is possible which makes it convenient to have a single manifold work for two concentration ranges. The sample is diluted, segmented with air and the stream is mixed. This stream is debubbled and a portion of this diluted sample is drawn through another pump tube to be the sample analyzed in the procedure. The manifold can be quickly changed to allow more sensitivity by disconnecting the dilution line. For use without dilution water should not be run through the dilution line and the sampler should be connected to the sample pump tube rather than to the pump tube to be used for dilution.

In the development of new analytical procedures and in the automation of existing methods, the analyst must determine the optimum concentrations of reagents. In manual procedures the analyst runs samples with several concentrations of the reagent being tested to determine the range of concentrations giving the same response. Using the proportioning pump of the AutoAnalyzer such studies may be made using a continuous concentration gradient of the reagent (62).

In such a study a concentrated solution of the reagent is pumped into a beaker containing a known volume of water. The solution in the beaker is mixed by a magnetic stirrer and the reagent is pumped from the beaker to the manifold at the same rate as the concentrated reagent pumped into the beaker. The concentration of the reagent in the beaker at time t is given by the equation

$$C_t = C_c\left(1 - e^{-\frac{rt}{v}}\right) \qquad \text{(VII-2)}$$

where

C_t is the concentration at time t

t is the time, in minutes

C_c is the concentration of the concentrated reagent being pumped into the beaker

r is the pumping rate, in ml/minute

v is the volume of liquid in the beaker, in ml

Since the pump tubes for input and output used in the system may not be precisely matched the test should be run over a short time.

D. Manifold Parts and Construction

To maintain, construct, or modify manifolds, the analyst must be familiar with the types of tubing and glass and plastic parts used in the construction of manifolds. This section will describe the use and connection of these parts of the manifold and other modules.

A plastic platter which fits snugly onto the pump is used to support the glass fittings and coils. The platter is easy to store and enables the system to be quickly changed from one procedure to another.

Pump tubes of three materials are available: standard clear plastic, solvaflex yellow plastic, and acidflex which is black. Liquid compatability with the various types of tubing is indicated in Table VII-3. Liquids which are incompatable with any of the types of tubing may be pumped using a displacement bottle. Water or another immiscible liquid is pumped into a closed bottle containing the incompatable liquid which is then carried by glass or other inert tubing to a fitting where it will be diluted by sample or reagent. For the transmission of liquids between fittings and modules and between reagent bottles and pump tubes, Tygon tubing, 1/16 inch I.D. x 1/8 inch O.D., is generally used. For the sample line the 0.034 inch probe is attached to 0.025 inch I.D. Tygon tubing. This tube is connected to pump tubes 0.051 inches or larger with a N7 nipple (Figure VII-6) and to smaller pump tubes with a N8 nipple.

Pump tubes are held in position with plastic end blocks which can hold as many as 15 tubes. The plastic shoulders on standard or solvaflex pump tubes and N9 nipples on acidflex tubes keep the tubes properly positioned. The end blocks are held in position by pins on the pump. As the tubes begin stretching and cannot be held taut, the end blocks should be moved to maintain tautness of the tubes.

Nipples are used to connect tubing to tubing and tubing to glass. If the tubing does not fit onto the nipple, the tubing can easily be stretched with a hemostat. To connect two tubes 0.056 inches or larger use a N9 nipple, to connect a tube 0.056 inches or larger with one 0.045 inches or smaller use a N7 nipple, and for

Table VII-3. RECOMMENDED TUBING FOR SPECIFIC CHEMICALS

Acetaldehyde, dilute	clear Standard
Acetic Acid 95%, Water 5%	Acidflex
Acetone	displacement bottle
Acids, Mineral (except hydrofluoric)	
dilute	clear Standard or Acidflex
concentrated	Acidflex
Amyl Acetate	displacement bottle
Aqueous Solutions	clear Standard
Benzene	Acidflex
Carbon Dioxide (gas)	clear Standard
Carbon Tetrachloride	Solvaflex
Chloroform	Acidflex
Dioxane	displacement bottle
Ethyl Alcohol	Solvaflex
Formaldehyde	clear Standard
Gasoline	Solvaflex
Glycerine	clear Standard
Glycol	clear Standard
Isopropyl Alcohol	Solvaflex
Methyl Alcohol	Solvaflex
Methyl Cellosolve, 65%	Solvaflex
Octane	Solvaflex
Pyridine	displacement bottle
Sodium Hydroxide	clear Standard
Styrene	Acidflex
Toluene	Acidflex
Trichloroacetic Acid	Acidflex
Water	Standard
Xylene	Acidflex

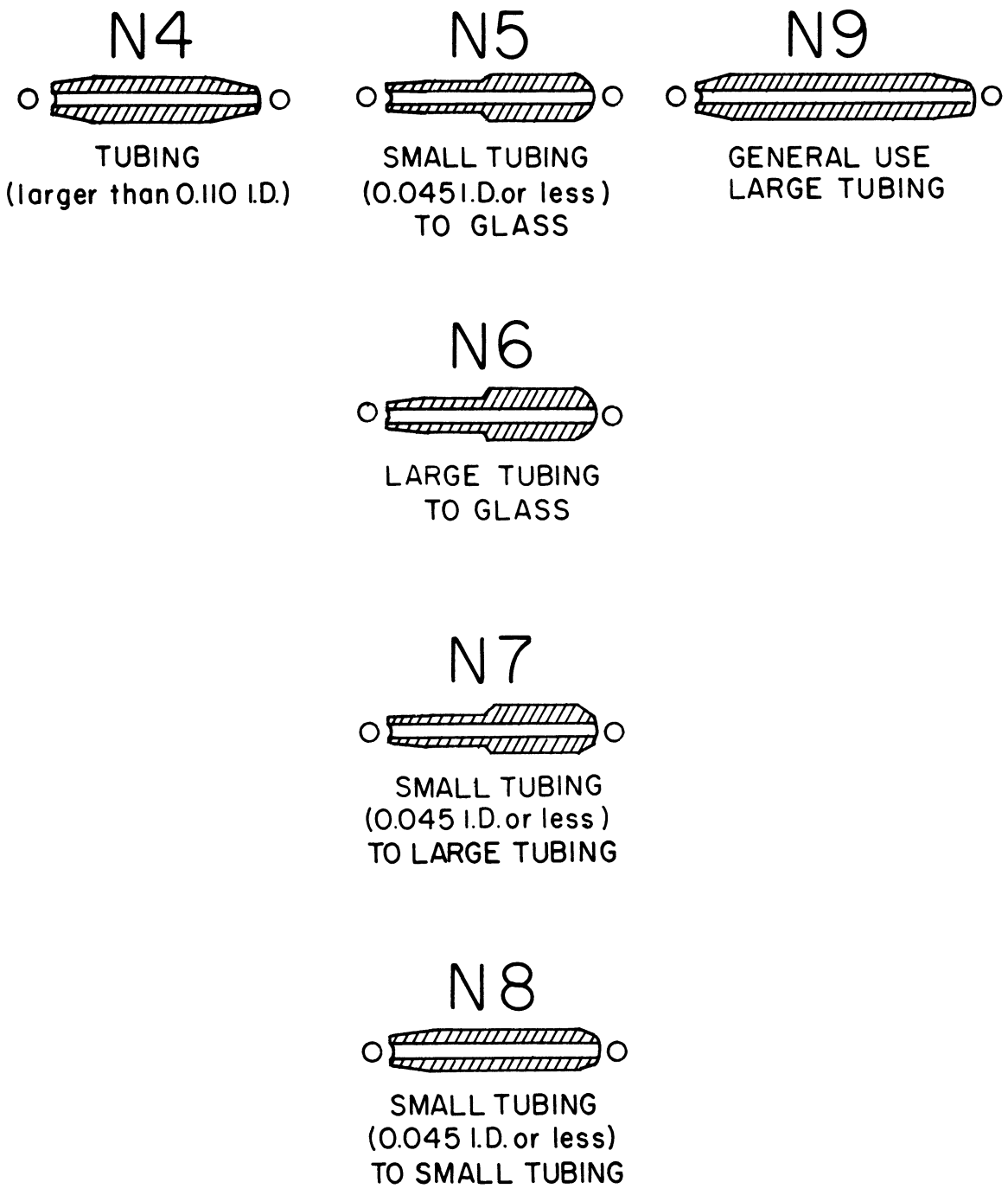


Figure VII-6. Frequently used AutoAnalyzer plastic fittings.

two tubes 0.045 inches or smaller use a N8 nipple. N5 nipples are used to connect tubing smaller than 0.045 inches and N6 nipples are used to connect 0.051 inch or larger tubing to glass. The wide portion of the fitting is slipped into a 2 cm length of 1/8 inch I.D. x 1/4 inch O.D. Tygon tubing and the Tygon sleeve and nipple is slipped over the glass until the flat end of the niple is butted against the glass. Two pieces of glass tubing can be joined using a piece of Tygon sleeving. The ends of the glass should form a butt joint.

Where it is necessary to use polyethylene tubing, the polyethylene tube should be slipped into an appropriate diameter Tygon tube and the two tubes should be sealed with cyclohexanone.

Glass fittings are used to join two or more liquid streams. The arms of these fittings are either capillary or regular bore. Liquid streams delivered by pump tubes 0.045 inches or less are connected to capillary arms while liquids delivered by larger pump tubes are connected to regular bore arms. Air lines are always connected to capillary bore arms. The H series of fittings are used to connect three streams and both the D and A series are used to join two streams.

Many types of mixing coils are available. Regular tubes (2.4 mm I.D.) are normally used, but with high flow rates 3.4 mm I.D. coils may be needed for effective mixing. With the large bore tubing air segmentation of the liquid must be from a 0.065 inch I.D. or larger pump tube. Jacketed mixing coils to cool streams emerging from the heating bath and coils with reagent inlets at the end or center of the coil are available.

Liquid-liquid extractions may be performed on the AutoAnalyzer, but it is, of course, impossible to use a high ratio of aqueous to organic phases. Extraction efficiency can be improved by using mixing coils containing glass beads. These coils are available in single and double length with or without water jackets. Phases may be separated using a B4 glass fitting or the phase separator described by Hadley (30).

E. Analytical Methods

This section is devoted to the automated analysis of specific substances in natural water. When authors have published a method in the Technicon symposia as well as in a scientific journal, the Technicon symposia will always be cited because of its availability. Only one procedure will be shown for many substances although numerous slightly modified procedures exist in the literature. Only colorimetric procedures will be discussed at length, but Auto-Analyzers have been adapted for use with other analytical methods Fluorometers and flame photometers are available from Technicon. Flame emission and atomic absorption photometers can easily be adapted to the AutoAnalyzer by use of a debubbler, as described by Klein, et.al.(48). The AutoAnalyzer may function simply to automatically supply samples or it may also dilute the sample or add materials such as lanthanum to supress the interference of other ions present in the sample. The AutoAnalyzer has been adapted for automated polarographic analysis of discrete samples by Lento (50). The system removes oxygen from the sample and adds supporting electrolyte and maximum suppressor. The polarograph is operated at a constant potential on the limiting current plateau and the diffusion current is measured as the sample flows through the cell. The automatic electrochemical determination of calcium and magnesium has been described by Fleet, Win and West (24). By use of a series of valves EDTA (ethylenediamine tetraacetic acid) or EGTA (ethylene glycol bis-β-aminoethyl ether)-N,N'-tetraacetic acid) is added to distilled water or the sample. The decrease in the anodic wave of EDTA is proportional to the sum of calcium and magnesium while the decrease in the anodic wave of EGTA is due only to the calcium.

1. Ammonia Most automated methods for the determination of ammonia utilize the alkaline phenol-hypochlorite reaction. This was first applies to automated analysis by Logsdon (51). Britt (14) used the method to monitor ammonia in the heavy water (D_2O) of a nuclear reactor, and O'Brien and Fiore (59) used it in the analysis of sewage. It is believed that the

colored product is an indophenol compound formed by the reaction (21)

$$NH_4^+ + OCl^- \longrightarrow NH_2Cl \xrightarrow{\text{Phenol}} OC_6H_4NCl \xrightarrow{\text{Phenol}}$$

$$OC_6H_4NC_6H_4OH \xrightarrow{OH^-} OC_6H_4NC_6H_4O^- \qquad \text{(VII-3)}$$

Flow diagrams for the determination of ammonia have been reported by Gaddy (25), Davies and Taylor (18) and Anderson, et al (3). Whitehead, et al (72) have modified the method to allow solids to be separated by a "T" fitting and added EDTA to prevent precipitation at the high pH of the reaction. The method can be modified by the addition of nitroprusside to catalyze the reaction and therefore enhance the sensitivity as suggested by Weatherburn (71). Using a 5 cm flow cell, a range of 0-2 ppm N can be achieved without range expansion.

Grasshoff (29) has automated a procedure using the intermediate reaction product of hypobromite and ammonia to oxidize iodide which is determined as its blue starch complex. Sawyer and Grisley (64) have used o-tolidine to determine the chloramine formed by the reaction of ammonia and hypochlorite.

2. Chloride Chlorides may be determined colorimetrically by reacting the sample with mercuric thiocyanate which forms unionized mercuric chloride and thiocyanate ions. The thiocyanate is reacted with ferric ion producing highly colored ferric thiocyanate proportional to the chloride in the original sample.

$$2Cl^- + Hg(SCN)_2 \longrightarrow HgCl_2 + 2SCN^- \xrightarrow{Fe^{+3}} Fe(SCN)^{+2} \qquad \text{(VII-4)}$$

O'Brien (57) has used this method with a dialyzer for the removal of solids for the determination of 0.5 to 1,000 ppm

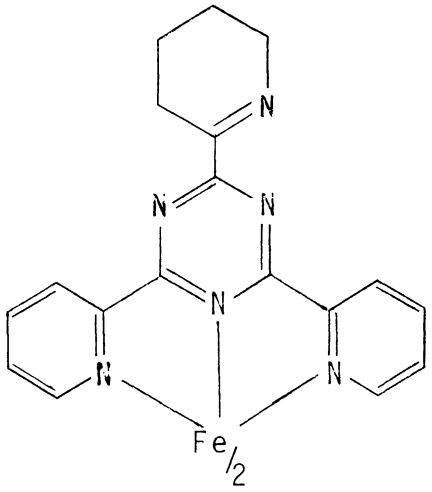
chloride in sewage. Britt (24) and Gaddy (25) developed chloride methods with a sensitivity of 5 ppb using 10x range expansion. Davies and Taylor's method (18) for river water uses a dialyzer for the removal of suspended solids. The reported range is 10 to 2,000 ppm using a 15 mm flow cell. Henriksen (39) developed a method for chlorides in the range 0 to 50 ppm and Anderson et al (3) have developed a procedure for 0 to 500 ppm chloride in sanitary and storm sewer water using a continuous filter to remove solids. In Kahn's method (42) mercuric ions are added to tie up a portion of the thiocyanate released by the chloride in the sample. By controling the amount of mercuric ion and using a dilution, the method is able to determine chloride in the range 30 to 30,000 ppm.

3. Chemical Oxygen Demand (COD) Organic matter in natural water may be determined by oxidation with dichromate. Organic compounds are oxidized to carbon dioxide and water while the dichromate (Cr^{+6}) is reduced to Cr^{+3}. Hexavalent chromium is orange while trivalent chromium is green. The COD may be measured by measuring either valence of chromium. The absorbance at 600 mμ due to Cr^{+3} will increase with increasing COD while at 425 mμ the absorbance will decrease since the unreacted Cr^{+6} is being measured. Automated methods based on the measurement of both Cr^{+3} and Cr^{+6} and using the continuous digestor or a high temperature heating bath ($155^{o}C$) have been proposed.

Adelman (1) has proposed an automated method using a heating bath and measuring the Cr^{+3} produced by the oxidation of the organic matter. By adjusting the ratio of sample to mercuric ion, which is used to suppress chloride interference, the procedure can analyze COD in a range from 0 to 150 ppm (using 4x range expansion and no sample dilution) or from 0 to 42,000 ppm (without range expansion and using a tenfold sample dilution). A procedure using the continuous digestor and measuring Cr^{+3} has been reported by Wagner (70). Ickes, et al (40) have reported procedures using both continu-

ous digestors and 155°C heating baths. Adelman (2) has reported a modification to cover the range 0-20 ppm COD.

4. Iron Most natural waters contain low concentrations of iron due to the insolubility of ferric ion, which is the predominant form of iron in oxygenated waters. Most methods for the analysis of iron make use of the intensely colored chelates formed with ferrous iron and 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline), 2,4,6-tripyridyl-s-triazine (TPTZ), 2,2'-bipyridine, or syn-phenyl-2-pyridyl ketoxime (20). Automated procedures (14,25,39,35,61) have generally used TPTZ as the ligand. The structure of the complex formed is (20)



Less sensitive procedures utilizing the colored complex of ferric ion and thioglycolic (mercaptoacetic) acid (8) and the complex of ferric iron and thiocyanate (7) have been reported.

5. Nitrite The conventional procedure of diazotization and coupling by the Greiss-Ilosvay method or one of its modifications is used for the determination of nitrite. With sulfonilamide and N-1-naphthylethylenediamine as reagents, the reactions are

$$NO_2^- + NH_2C_6H_4SO_2NH_2 + 2H^+ \rightarrow N^+\equiv NC_6H_4SO_2NH_2 + 2H_2O \qquad \text{(VII-5)}$$

$$N^+\equiv NC_6H_4SO_2NH_2 + C_{10}H_7NHCH_2CH_2NH_2 \rightarrow \begin{matrix} N \\ \| \\ NC_{10}H_6NHCH_2CH_2NH_2 \end{matrix} C_6H_4SO_2NH_2 + H^+$$

A useful review of spectrophotometric methods for the determination of nitrite has been published by Sawicki, et al (63). Procedures for nitrite have been reported by Britt (14), O'Brien and Fiore (58), Gaddy (25), Henriksen (34), and Kamphake, Hannah, and Cohen (45).

6. Nitrate An automated brucine method has been reported by Kahn and Brezenski (43) for 0.05 to 0.6 mg NO_3-N per liter in estuarine waters. Most AutoAnalyzer procedures for the determination of nitrate are based on manual methods using hydrazine and a copper catalyst (56), amalgamated cadmium filings (55), or a cadmium-copper couple (74) to reduce nitrate to nitrite, followed by colorimetric analysis of the nitrite. Automated methods using amalgamated cadmium and a cadmium-copper couple for reduction have been reported by Bernhard and Macchi (5) and Armstrong and LaFond (4) respectively. Brewer, Chan, and Riley (12) and Henriksen (39) have used cadmium filings to reduce nitrate to nitrite. Several investigators have automated the hydrazine method (14,25,18,34). The hydrazine reduction method of Kamphake et al (45) eliminates the acetone used to destroy excess hydrazine and employs a temperature at which equivalent absorbances are obtained for equimolar nitrate and nitrite standards. The true concentration of nitrate nitrogen is the apparent concentration minus the concentration of nitrite nitrogen.

7. Kjeldahl Nitrogen The development of the continuous digestor has permitted the complete automation of the Kjeldahl procedure for the determination of the nitrogen of organic compounds. The digestion process in the continuous digestor

has recently been reviewed (23). The high temperature of the thin film of sample on the wall of the helix permits the digestion to be completed in a few minutes rather than the hours required in a Kjeldahl flask where the sample temperature does not exceed the boiling point of the liquid. In methods for the determination of nitrogen (15,53,66,44) the sample, acid, and catalyst to permit the digestion of refractory nitrogen compounds, are pumped into the digestor. Following digestion, water is added and the sample is pulled by a second pump into a small mixing chamber and then to a second manifold where the ammonia is determined by the alkaline phenol-hypochlorite method. Kammerer, et al (44) have found that the use of 0.01M sodium nitroprusside to dilute the sample after digestion results in a five fold increase in sensitivity.

8. Manganese Henriksen published a method for the determination of 0.02-1.0 mg manganese per liter using a 1.5 cm flow cell (39,37). The reaction of formaldoxime ($H_2C = NOH$) and manganese in alkaline solution produces the reddish-brown soluble product $(CH_2NO)_3Mn$. The interference of iron is eliminated by adding iron and decomposing the iron formaldoxime complex with EDTA and hydroxylamine hydrochloride.

9. Phosphate One of the most important analyses in pollution or productivity studies is the analysis of phosphate. Phosphate is present in many forms in water; commonly the analyst will be called upon to analyze for inorganic phosphate, total soluble phosphate and total phosphate. These differentiations are made by filtering and acid digestion of the sample. The phosphate is complexed with molybdate at a pH where silicomolybdate is not formed and the phosphomolybdate is reduced to an intensely blue compound whose absorbance is then measured. Commonly used reducing agents include aminonaphthol sulfonic acid, hydrazine, stannous chloride, and ascorbic acid.

Manual and automated methods using ascorbic acid employ

potassium antimonyl tartrate to catalyze the reduction. These procedures are sensitive to less than 10 µg phosphorus per liter. Procedures have been automated using ascorbic acid as one reagent and sulfuric acid, ammonium molybdate, and potassium antimonyl tartrate as the second (74,28), while other procedures use a single mixed reagent which is prepared daily (12,17). Grasshoff (29,27) has automated a digestion procedure for the determination of organic phosphates. The digestion is achieved by pumping the sample through a quartz coil surrounding a high intensity UV lamp. An automated procedure using a persulfate digestion at 125°C and 3.5 atmospheres pressure has been reported (6). Excess ascorbic acid was added to react with the large amounts of chlorine released from seawater samples. Alcohol has been added to extend the concentration range of the method (54).

Stannous chloride reduction methods have been reported by Gaddy (25), Lee (49), and Gales and Julian (26). Gales and Julian also describe a manual digestion procedure for total phosphate compatable with the automated analysis. Henrikson (39,33) reported an automated method based on the extraction of the phosphomolybdate with isobutanol and subsequent reduction with stannous chloride. In a later paper (36) the reagent concentrations were altered to eliminate silica interference. The stannous chloride reduction may be eliminated for the analysis of sewage and highly polluted waters (39,38). It has been reported (17) that consistant results were not obtained using Henrikson's method (33).

Two hydrazine reduction methods for inorganic phosphates have been reported (3,7) and a procedure for total phosphate using the continuous digestor to hydrolyze the sample with persulfate and concentrated sulfuric acid has been reported (7).

Davies and Taylor (18) dialyzed the sample into aminonaphthol sulfonic acid and added acidified molybdate and found a useful concentration range of 0.5-50 ppm. Manual digestion has been used prior to an analysis using aminonaphthol sulfonic acid as a reductant (10).

10. Silica In all methods (39,61,4,28,73,60,13) silica is determined by complexation with acidified molybdate to form a silicomolybdate complex which is reduced to an intense heteropolyblue. Oxalic or tartaric acid is added prior to the reduction to destroy any phosphomolybdate. All procedures are sensitive to low ppb concentrations and dilution of the sample may be necessary for samples of many natural waters.

11. Other Analyses Many other analyses have been adapted to the AutoAnalyzer including boron (19,41), cyanide (69), iodine (46), magnesium (24,47), alkalinity (18), hardness (18,32), sulfate (22), permanganate value (35), and fluoride (25,28,11, 16,31). A distillation column for use with AutoAnalyzer manifolds has been used in the automated determination of fluoride and phenol (16,52). The determination of copper, chromium, nickel, zinc, and cadmium in wastewaters is described by Berry (8). Automated colorimetric methods have been published for chromium (25) and copper (39). Analyses for many other water constituents have been automated (65).

REFERENCES

1) M. H. Adelman, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 552.

2) M. H. Adelman, Paper presented at 18th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, 1967.

3) J. J. Anderson, O. E. Bruss, L. A. Hamilton, and M. L. Robins, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. I, Mediad, New York, N.Y., 1968, p. 373.

4) F. A. J. Armstrong and E. C. LaFond, Limnol. and Ocean., 11, 538 (1966).

5) M. Bernhard and G. Macchi, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 255.

6) M. Bernhard, E. Torti, and G. Rossi, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. II, Mediad, New York, N.Y., 1968, p. 395.

7) H. Bernhardt and A. Wilhelms, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. I, Mediad, New York, N.Y., 1968, p. 385.

8) A. J. Berry, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 560.

9) W. J. Blaedel and R. H. Laessig, "Advances in Analytical Chemistry and Instrumentation," Vol. 5, C. N. Reilley and F. W. MCLafferty, Eds., Interscience Publishers, New York, N.Y., 1966, p. 69.

10) D. R. Blaisdell, B. Compton, and J. H. Nair, III, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. I. Mediad, New York, N.Y., 1968, p. 393.

11) S. Bonk and L. N. Scharfe, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 638.

12) P. G. Brewer, K. M. Chan, and J. P. Riley, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 308.

13) P. G. Brewer and J. P. Riley, Anal. Chim. Acta, 35, 514 (1966)

14) R. D. Britt, Jr., Anal. Chem., 34, 1728 (1962).

15) E. W. Catanzaro, G. R. Goldgraben, and R. M. Gasko, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N. Y., 1966, p. 241.

16) K. M. Chan and J. P. Riley, Anal. Chim. Acta, 35, 365 (1966).

17) K. M. Chan and J. P. Riley, Deep-Sea Res., 13, 467 (1966).

18) A. W. Davies and K. Taylor, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 294.

19) T. F. Demmitt, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 204.

20) H. Diehl and G. F. Smith, "The Iron Reagents: Bathophenanthroline, Bathophenanthroline-Disulfonic Acid, 2,4,6-Tripyridyl-S-Triazine, Phenyl-2-Pyridyl Ketoxime," 2nd Ed. Revised, G. Frederick Smith Chemical Company, 1965.

21) A. C. Docherty, Paper presented at Technicon International Symposium, New York, N.Y., 1964.

22) L. W. Ferrara, R. S. Floyd, and R. W. Blanchar, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 109.

23) A. Ferrari, E. Catanzaro, and F. Russo-Alesi, Ann. N.Y. Acad., Sci., 130 (2), 602 (1965).

24) B. Fleet, Soe Win, and T. S. West, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. II, Mediad, New York, N.Y., 1968, p. 355.

25) R. H. Gaddy, Jr., "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y. 1966, p. 210.

26) M. E. Gales, Jr. and E. C. Julian, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 557.

27) K. Grasshoff, Zeit. Anal. Chem., 220, 89 (1966).

28) K. Grasshoff, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 304.

29) K. Grasshoff, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 573.

30) F. C. Hadley, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 383.

31) J. E. Harwood, Water Res., 2, 637 (1968).

32) A. Henriksen, Vattenhygien, 21, 58 (1965).

33) A. Henriksen, Analyst, 90, 29 (1965).

34) A. Henriksen, Analyst, 90, 83 (1965).

35) A. Henriksen, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 301.

36) A. Henriksen, Analyst, 91, 290 (1966).

37) A. Henriksen, Analyst, 91, 647 (1966).

38) A. Henriksen, Analyst, 91, 652 (1966).

39) A. Henriksen, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 568.

40) J. H. Ickes, E. A. Gray, N. S. Zaleiko, and M. H. Adelman, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. I, Mediad, New York, N.Y., 1968, p. 351.

41) H. James and G. H. King, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. II, Mediad, New York, N.Y., 1967, p. 123.

42) L. Kahn, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. I, Mediad, New York, N.Y., 1968, p. 369.

43) L. Kahn and F. T. Brezenski, Environ, Sci. and Tech., 1, 492 (1967).

44) P. A. Kammerer, M. G. Rodel, R. A. Hughes, and G. F. Lee, Environ. Sci. and Tech., 1, 340 (1967).

45) L. J. Kamphake, S. A. Hannah, and J. M. Cohen, Water Res., 1, 205 (1967).

46) H. E. Keller, D. Doenecke, and W. Leppla, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. II, Mediad, New York, N.Y., 1968, p. 371.

47) P. W. Kelley and F. D. Fuller, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 266.

48) B. Klein, J. H. Kaufman, and S. Morgenstern, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 10.

49) G. E. Lee, "Chemical Environment in the Aquatic Habitat," H. L. Golterman and R. S. Clymo, Eds., N.V. Noord-Hollandsche Uitgevers Maatschapij, Amsterdam, 1967, p. 169.

50) H. G. Lento, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 598.

51) E. E. Logsdon, Ann. N.Y. Acad. Sci., 87 (1), 801, (1960).

52) J. F. Marten and D.R. Grady, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, 1967, p. 546.

53) W. H. McDaniel, R. N. Hemphill, and W. T. Donaldson, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. I, Mediad, New York, N.Y., 1968, p. 363.

54) A. H. Molof, G. P. Edwards, and R. W. Schneeman, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 245.

55) A. W. Morris and J. P. Riley, Anal. Chim. Acta, 29, 272 (1963).

56) J. B. Mullin and J. P. Riley, Anal. Chim. Acta, 12, 464 (1955).

57) J. E. O'Brien, Wastes Eng., 33, 670 (1962).

58) J. E. O'Brien and J. Fiore, Wastes Eng., 33, 238 (1962).

59) J. E. O'Brien and J. Fiore, Wastes Eng., 33, 352 (1962).

60) R. Place and F. Hardy, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 649.

61) G. Rudnik, "Automation in Analytical Chemistry; Technicon Symposia 1965," Mediad, New York, N.Y., 1966, p. 220.

62) A. L. Ryland, W. P. Pickhardt, and C. D. Lewis, Paper presented at Technicon International Symposium, New York, N.Y., 1964.

63) E. Sawicki, T. W. Stanley, J. Pfaff, and A. D. Amico, Talanta, 10, 641 (1963).

64) R. Sawyer and L. M. Grisley, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. I, Mediad, New York, N.Y., 1968, p. 347.

65) Technicon Corporation, Tarrytown, N.Y., 10591.

66) A. M. Tenny, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, N.Y., 1967, p. 580.

67) R. E. Thiers, R. R. Cole, and W. J. Kirsch, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. I, Mediad, New York, 1967, p. 37.

68) R. E. Thiers and K. M. Oglesby, Clin. Chem., 10, 246 (1964).

69) J. H. Vought, Plating, 52 (5), 420 (1965).

70) R. Wagner, "Automation in Analytical Chemistry; Technicon Symposia 1966," Vol. II, Mediad, New York, N.Y., 1067, p. 133.

71) M. W. Weatherburn, Anal. Chem., 39, 971 (1967).

72) R. Whitehead, G. H. Cooke, and B. T. Chapman, "Automation in Analytical Chemistry; Technicon Symposia 1967," Vol. II, Mediad, New York, N.Y., 1968, p. 377.

73) A. L. Wilson, Analyst, 90, 271 (1965).

74) E. D. Wood, F. A. J. Armstrong, and F. A. Richards, J. mar. biol. Ass. U.K., 47, 23 (1967).

VIII ANALYSIS FOR MAJOR PHYSICAL CHARACTERISTICS

Major pnysical characteristics of natural and wastewaters may be arbitrarily classified as

(a) density and viscosity,

(b) temperature,

(c) electrical conductivity,

(d) turbidity,

(e) particulate, volatile and dissolved matter,

(f) oils, grease and other immiscible liquids,

(g) color, and

(h) odor

A. Density and Viscosity:

There is a scarce of information in the literature on the application of density,viscosity and surface tension measurements for water quality characterization.

This probably results from the fact that the latter of these tests is not frequently performed, and the procedures for the first two are rather straightforward.

Differences between absolute density and specific gravity, and the effect of temperature and salinity on these parameters, have been discussed by Cox. (1) Density determinations are of particular interest for characterization of brine wastes, for which concentrations of dissolved materials are commonly indicated by density measurements.

Density measurements of high-salinity wastewaters are also significant for relating concentration on a weight basis to concentration on a volume basis. By definition, concentration expressed in terms of parts per million represents the weight of dissolved matter per one million equal weights of solution (i.e., milligrams of solute per kilogram of solution). A concentration of 1,000 ppm will increase the density of solution by only approximately 0.1 percent, which may not be significant. At high concentrations, however, corrections must often be made to account for changes in density. The U.S. Geological Survey (2) has arbitrarily selected a concentration level of 7,000 ppm, below which corrections for changes in density are not necessary.

Density determinations may be accomplished by measuring the weight of an exact volume of solution at a given temperature, commonly 20^{o}C (the same temperature at which volumetric glassware is calibrated). Results are accurate to 10.0005 g. (2) More commonly, density is measured with a hydrometer, at the temperature

of the sample with appropriate correction to 20°C. Nomographs are usually provided to facilitate conversion.

Viscosity is a direct measure of the resistance of the liquid to flow or fluidity, which is of interest for certain industrial wastewaters of high solid content, waste slurries, and sludges. Results are usually expressed in centipoise units at 20°C. The viscosity of pure water is taken to be approximately equal to unity at 20°C (1.009 centipoise).

Several instruments are available for viscosity determinations, e.g., the canal viscometer (Ostwald) or the couette viscometer (or Brookfield viscometer). Viscosity can also be measured by determining the time of fall of a spherical ball of known weight and dimension through a column of the test solution. ((3,2)

B. TEMPERATURE

Temperature is an intensive measure, and should not be confused with the extensive property of heat capacity. Measurement of temperature in industrial waste effluents is of particular importance in cases where biochemical activity in the receiving water or the heat budget of the stream are matters of concern. Such is the case with waste cooling waters from the power industry, which may cause significant thermal pollution of receiving streams.

Liquid-in-glass thermometers, in which mercury is often used, are the simplest temperature measuring devices. The

response time of such simple thermometers is one of the longest of common temperature measuring devices. Needless to say, liquid-in-glass thermometers are not very suitable for continuous monitoring systems. In certain cases differential temperature measurements are more significant than absolute values, and a number of commercially available thermometers can be employed.

Other temperature measuring devices include bimetallic thermometers, radiation pyrometers, resistance thermometers, thermistors, and thermocouples. An excellent discussion of the application of temperature transducers for environmental measurements has been presented by Bollinger. (4)

C. ELECTRICAL CONDUCTIVITY

Electrical conductivity has been conveniently used as a measure of the total concentration of ionic species in a water sample. (5) Much confusion exists in the literature regarding interpretation of conductivity data, and the calibration of conductivity salinometers. The electrical conductance, L, of a solution can be represented by the expression

$$L = K_c \sum_i^n C_i \lambda_i Z_i \qquad \text{VIII-1}$$

where K_c is a constant, characteristic of the geometry and size of the conductance cell, C the molar concentration of the individual ions in solution, λ the equivalent ionic conductance, and Z the ionic charge. Thus the electrical conductance will vary with the number, size, and charge of the ions, and also with

some solvent characteristics such as viscosity. For this reason a meaningful comparison of the electrical conductance of two different types of industrial wastewaters may be difficult. Equality in electrical conductance may not mean equality in total dissolved solids. Nonetheless, conductance measurements can be used to good advantage for continuous monitoring of the strength of a given wastewater. In this case a change in conductance may be assumed to be due to a change in the number of ions rather than a change in the type of ions.

Conductance measurements are used extensively for monitoring the quality of surface waters, (6) and in chemical oceanography for salinity determinations. (1)

Conductivity determinations are usually based on alternating current measurements using either electrodes or inductive systems, depending on how the current is generated in solution. In the more conventional system of the former type, measurement is based on the application of an alternating current (or a.c. potential difference) across two or more electrodes immersed in the test solution. The major disadvantages of this type of system are the possibilities for polarization and poisoning (fouling) of the electrodes. In systems of the second type, the electrodes do not come in contact with the test solution, but are isolated by a layer of glass or some other dielectric (insulating) material. A very high frequency current in the megacycle-per-second range is used. In such systems the conductivity cell represents a series combination of a capacitance (the dielectric material separating the electrodes from the solution) and a

parallel-connected capacitance and resistance (the solution capacitance and resistance, respectively). Although the cell response is less direct because the electrodes are not in contact with the solution, the problems of electrode fouling and polarization are eliminated. Conductivity measurements based on high frequency inductive systems are fundamentally more sound than those based on conventional electrode systems, and eventually will gain wider acceptance for laboratory and field applications. (1)

It should be noted that one of the basic problems in precision conductivity is temperature control. Temperature effects on ionic conductance in heterogenous solutions are quite complex. The temperature coefficient for a solution of constant ionic strength, varies with temperature. The conductivity of sea water, for example, increases by 3% per degree increase in temperature at $0^{o}C$ and only 2% per degree increase at $25^{o}C$. At $30^{o}C$ the conductivity of a solution is about double the value at $0^{o}C$. Likewise, the temperature coefficient of conductivity for sea water varies appreciably with large variations in ionic strength. (1, 7) In oceanographic work, therefore, relative conductance is determined rather than absolute conductance. In this case the ratio of the conductance of the sample to that of a reference solution at the same temperature is measured. In certain modifications, a thermistor or a resistance is used instead of a reference solution. (1)

Conductivity measurements are quite well suited for <u>in situ</u> and continuous type analyses. Great care should be taken, however,

to account for changes in temperature, pressure, and other such factors.

D. TURBIDITY

Turbidity is a measure of the light scattering characteristics of a water, and is attributable to colloidal and particulate matter suspended in the water. Reference is to a standard suspension of fine silica. (8) The Jackson Candle Turbidimeter is the standard reference instrument for turbidity measurements. The Jackson turbidity test is based on measuring that length of light path through the solution at which the outline of the flame of a standard candle becomes indistinct. Results are reported in arbitrary turbidity units. (9,10)

Wastes of turbidity in excess of 1000 Jackson units are diluted prior to measurement. For waters of low turbidity (less than 25 Jackson turbidity units) nephelometric or light scattering techniques are most commonly used. (11, 8) Black and Hannah (11) have discussed the theoretical and procedural aspects of turbidity measurements with the Jackson Candle method and more sophisticated methods. A simple low-angle photometer that may be calibrated with clay suspensions in terms of Jackson turbidity units is described and recommended for use with low turbidity waters. Several commercial turbidity monitoring systems are available, and have found wide use for monitoring wastewater quality. (12)

E. PARTICULATE, VOLATILE AND DISSOLVED SOLIDS

Particulate suspended matter consists of fine, solid materials which are dispersed in water to give a heterogenous suspension. This material can be separated by filtration. Dissolved solids, on the other hand, consist of non-volatile compounds and salts in true solution, i.e., homogeneous phase. (13)

Particulate matter is usually determined by filtering a given volume of wastewater, extracting the residue with a solvent (carbon tetrachloride, benzene or chloroform), drying at 103°C, igniting at 180°C and weighing the final residue. (13)

Dissolved solids are determined by weighing the residue from the filtrate after evaporation and extraction with organic solvent and ignition at 180°C. (13)

Standard Methods for the Examination of Water and Wastewaters (13) classifies particulate, volatile and dissolved matter as follows: (a) residue on evaporation, (b) total volatile and fixed residue, (c) total suspended matter, and (d) dissolved matter. Although this classification is particularly suitable for domestic wastes and municipal sewage-treatment plant effluents, it is applied frequently to a variety of industrial waste effluents.

Residue on evaporation is determined by evaporating a given sample, drying at 103°C, and weighing the residue. Total volatile residue is determined by igniting the sample at 600°C after determining the residue on evaporation, and calculating the weight loss due to ignition. The weight of the residue after ignition is reported as total fixed residue.

The total suspended matter is the non-filterable residue and is determined by filtering a sample through a membrand filter or an asbestos mat in a Gooch crucible. The dry residue remaining after evaporation of the filtrate at 103°C is reported as dissolved matter of filterable residue. This can be also obtained by calculating the difference between the residue on evaporation and the total suspended matter. (13)

Analysis for residue in an industrial wastewater generally is of little direct value in estimating its effect on a receiving water. Residue determinations are p·obably more valuable for control of plant operation.

F. OILS, GREASE AND IMMISCIBLE LIQUIDS

The gross determination of volatile and nonvolatile oily material is of particular interest for industries such as oil refineries. (14) Tests for oils and grease are based on solvent extraction procedures, using common solvents such as hexane, petroleum ether, benzene, chloroform, or carbon tetrachloride. The amount of oily matter determined is primarily dependent on the type of solvent used and the extraction procedure. Needless to say, the test is not selective for immiscible oils and grease; other organic matter in solution (e.g., phenols, organosulfur compounds), will also be measured.

The procedure for determination of volatile and nonvolatile oily matter in wastewater is based on refluxing a given volume of sample and collecting the volatile oily matter, which is then

measured volumetrically. The reamining sample is extracted with an immiscible solvent. The extracts are distilled to remove the solvent, and the residue is weighed and reported in units of parts per million by weight. Oily matter, measured according to this procedure, is defined (14) as hydrocarbons, hydrocarbon derivatives and other fractions with a boiling point of 90°C or above which are extracted from water at pH 5.0, or lower, using benzene as a solvent. Various extraction techniques and equipment have been reported.

Nonvolatile oily material may also be determined by flocculation of the wastewater with an iron salt, followed by extraction of the oily matter from the flocs. The sample is first acidified to pH 4 and treated with an iron salt to form a flocculent ferric hydroxide precipitate in the sample. The floc separated from the sample by filtration and is then extracted with ether. The ether is then evaporated in a specially designed U tube with a calibrated capillary. (14) The oil is displaced into the graduated section of the tube and measured volumetrically.

An infrared spectrometric method for gross determination of volatile and nonvolatile oily matter has been described. (14 ,15) This method is based on extraction of the oily matter with carbon tetrachloride. By means of absorption measurements of the extract at 3.4 and 3.5 microns, the oily matter concentration is determined from calibration curves. This method is especially suitable for routine monitoring of effluents which are known to contain relatively constant amounts and types of oily matter. (14)

G. COLOR

It is customary to differentiate between true and apparent color in waters and wastewaters. True color is due only to matter which is in true solution, while apparent color includes the effects of matter in suspended and coloidal states as well.

The major problem associated with this aspect of the analysis of industrial wastewaters is how to define and express color. Classically, the color of a trade effluent has been determined by visual comparison with colored solutions of known concentration or with special colored glass discs. In laboratory operations, comparison is made to standard platinum-cobalt color solutions, and the standard unit of color is that produced by 1 mg of platinum per liter, in the form of chloroplatinate ion. For field use, comparison is made with colored glass discs calibrated to correspond to the platinum-cobalt scale. (16)

Color determinations by visual comparison are subject to a number of interferences and variables. The main drawback to this method is the subjectivity and variation in response of different individuals to color. It is obvious also that certain industrial wastes may produce colors which cannot be matched well by the standard platinum-cobalt scale.

A more accurate determination of color in wastewaters can be accomplished by application of tri-stimulus colorimetry techniques. (17, 18, 19) The color of a filtered waste can be expressed in terms which approximately describe the visual response of an individual. One of these terms relates to the brightness

of color, or luminosity. The hue of the color (e.g., red, yellow, green, etc.) is characterized in terms of a dominant wave length and the degree of saturation (pastel, pale, etc.) by purity. Luminosity and purity are usually reported in units of percent, and the dominant wave length in millimicrons.

Tri-stimulus parameters are commonly determined from measurements of the light transmission characteristics of a filtered sample of wastewater. Transmission data are converted to color classification terms by using standards adopted by the International Commission on Illumination. (18) Chromaticity diagrams are used to describe the color numerically in terms of the tri-stimulus parameters. (13)

Trichromatic color characteristics of filtered wastewater are measured with ordinary absorption spectrophotometers. A photometric technique has been proposed for routine work. (13) This method is based on the use of three special tri-stimulus light filters which, when combined with a specific light source and photoelectric cell in a filter photometer, will give effective energy distribution curves similar in shape to the "CIE" tri-stimulus curves when weighted with illuminant "C". (17)

H. ODOR

Odor, like color, is a measure of a physiological response. (20 , 21, 22) Determination of odor is based solely on the olifactory senses of the analyst, or on those of a group of individuals, and on the ability of the analyst (or group) to

distinguish between different levels and kinds of odors. The testing is based entirely on arbitrary comparison since no absolute units or base for odor exist. (8, 14)

Several authors have attempted to characterize and classify the origin of odor in wastewaters. (20, 8, 23, 24, 25, 26) Most of these studies treat taste and odor as closely connected human responses. Taste determinations are generally not recommended for wastewater or untreated industrial effluents, and thus are excluded from the present discussion.

Odor can always be related to the presence of volatile organic and/or inorganic species present in water. Odor intensity is a function of the volatility and the concentration of the odor-causing species, as well as of certain environmental factors such as temperature, ionic strength and pressure. It has been claimed that there are only four basic types of odor: (a) sweet, (b) sour, (c) burnt, and (d) goaty, realizing that the many odors are in fact combinations of two or more of these groups.

Odors often can be related to the presence of certain biological forms in the wastewater, such as algae and actinomycetes. Such odor-causing organisms are believed to secrete characteristic volatile oils during growth, and upon decomposition and decay. Such poetic terms as musty, earthy, woody, moldy, swampy, grassy, fishy, and wet-leaves have been used to describe odors. (20, 24) Odors have also been classified by chemical type (8) as shown in Table VIII-1

TABLE VIII-1 ODORS CLASSIFIED BY CHEMICAL TYPES

Odor Class	Chemical Types Included	Odor Characteristics				Odors and Algae and Fungi
		Fragrance	Acidity	Burntness	Caprylicness	
Estery	Esters	High	Med.	Low to Med.	Med.	. . . .
	Esters					
	Lower ketones					
Alcoholic	Phenols and cresols	High	Med. to High	Low to High	Med.	Asterionella Coelosphaerium
	Alcohols					
	Hydrocarbons					
Carbonyl	Aldehydes	Med.	Med.	Low to Med.	Med.	Mallemonas
	Higher ketones					
Acidic	Acid anhydrides	Med.	Very High	Low to Med.	Med.	Anabaena
	Organic acids					
	Surfur dioxide					
Halide	Quinones	High	Med. to High	Med. to High	Low to High	Dinobryon Actinomycetes
	Oxides (including ozone)					
	Halides					
	Nitrogen Compounds					

TABLE VIII-1 CLASSIFICATION - - - - - - (cont.)

Odor Class	Chemical Types Included	Odor Characteristics				Odors and Algae and Fungi
		Fragrance	Acidity	Burntness	Caprylicness	
Sulfury	Selenium compounds	Med.	Med.	Very High	Very High	Aphanizomenon
	Arsenicals					
	Mercaptans					
	Sulfides and hydrogen sulfide					
Unsaturated	Acetylene derivatives	High	Med.	Med.	High	Synura
	Butadiene					
	Isoprene					
	Vinyl monomers					
Basic	Higher amines	High	Med.	Low to Med.	High	Uroglenopsis
	Alkaloids					Dinobryon
	Ammonia and lower amines					

Recent studies of odor characteristics and human response have led to a proposal of a steriochemical theory of odor (21, 27) This theory relates the response to odor to the geometty of molecules. It has been postulated that the olifactory system is composed of receptor cells of certain different types, each representing a distinct "primary" odor, and that odorous molecules produce their effects by fitting closely into "receptor sites" on these cells. This concept is similar to the "lock and key" theory used to explain certain biochemical reactions; e.g., enzyme with substrate, antibody with antigen, and desoxyribonucleic acid with ribonucleic acid in protein synthesis.

Seven primary odors are distinguished, (24) each of them by an appropriately shaped receptor at the olifactory nerve endings. The primary odors, together with reasonably familiar examples are (a) camphoraceous, e.g., camphor or moth repellent, (b) musky, e.g., pentadencanolactone as in angelica root oil, (c) floral, e.g., phenylethyl methyl ethyl carbinol as in roses, (d) pepperminty, e.g., menthone as in mint candy, (e) pungent, e.g., formic acid or as vinegar, and (g) putrid, e.g. butyl mercaptan as in rotton eggs.

It has been claimed that every known odor can be made by mixing the seven primary odors in certain combinations and proportions. (25)

Odors resulting from mixtures of two or more odoriferous substances are extremely complex. The mixture may produce an odor of greater or lesser intensity than might be expected from summing the individual odors, or a completely different kind of

odor may be produced. (27 , 24 , 25) Accordingly, it is frequently necessary to characterize the odor of the wastewater and that of the receiving stream both separately and in combination if the actual relationship and effect is to be determined.

Odor intensity is expressed in terms of the threshold odor number. (8, 14 , 13) By definition, the threshold odor number is the greatest dilution of the sample that still leaves a perceptible residual odor. The test procedure is based on successive dilution of a sample with odor-free water. disregarding any suspended matter or immiscible substances, until a dilution is obtained which has a barely perceptible odor. It has been recommended that odor tests be run at 25°C and 60°C (13) or 40°C and 60°C. (8) In all cases the sampling and test temperature should be reported, since the threshold odor is a function of temperature. A given sample, under fixed conditions, will emit a characteristic odor stimulus, but the response to this stimulus and the judgment based upon this response are purely subjective matters, and their interpretation may vary considerably from individual to individual. (27 ,25 , 26) Consequently, it is desirable to use a panel or group of judges, rather than a single analyst for both qualitative and quantitative evaluation of odors in water or wastewater samples. (8)

BIBLIOGRAPHY

1. Cox, R. A., "The Physical Properties of Sea Water," in Riley and Skirrows, "Chemical Oceanography I," Academic Press, New York, N.Y. Vol. I, pp. 73 (1965).
2. Rainwater, F. H., and L.L. Thatcher, "Methods for Collection and Analysis of Water Samples," U.S. Geological Survey Water, Supply Paper 1454 (1960).
3. Institution of Water Engineers, "Approved Methods for the Physical and Chemical Examination of Water," 3rd ed., W. Heffer & Sons, Ltd., Cambridge, England (1960).
4. Bollinger, L.E., Proc. Symposium Environmental Measurements - Valid Data and Logic Interpretations, Public Health Service Publication No. 999-AP-15, pp. 41 (1964).
5. Rossum, J.R., Anal. Chem., 21, 631 (1949).
6. Wilcox, L.V., J. Am. Water Works Ass., 42, 775 (1950).
7. Cox, R. A., Deep Sea Res., 9, 504 (1962).
8. American Society of Testing Material, "Manual on Industrial Water and Industrial Waste Water," American Society for Testing Materials, 2nd ed., (1964)
9. Baylis, J.R., Ind. Eng. Chem., 18, 311 (1926).
10. Palin, A.T., Water & Water Engr., 59 341 (1955)
11. Black, A.P., and S.A. Hannah, J. Amer. Water Works Ass., 57, 901 (1965).
12. Cleary, E.J., J. Am. Water Works Ass., 54 1347 (1962).
13. APHA, AWWA and WPCF, "Standard Methods - Water and Wastewater," American Public Health Ass., 12th ed. (1965).

14. American Petroleum Institute, "Manual on Disposal of Refinery Wastes - Methods for Sampling and Analyses of Refinery Wastes", American Petroleum Institute Publication, New York, N.Y. (1957).

15. Simard, R.G., I. Hasegawa, W. Bandaruk, and C.E. Headington, Anal. Chem., 23, 1384 (1951).

16. Degremont, E., "Memento Technique De L'Eau," Degremont, Paris, France (1959).

17. Jones, H., "The Science of Color," Thomas Y. Crowell Co., New York (1952).

18. Mellon, M. G., Analytical Absorption Spectroscopy, John Wiley & Sons, Inc., New York, Chap. 9 (1950).

19. Rudolfs, W., and W.D. Hanlon, Sewage Ind. Wastes, 23, 1125 (1951).

20. Fair, G.M., J. New Engl. Water Works Ass., 47 248 (1933).

21. Gerald, F.A., "The Human Senses," John Wiley & Sons, Inc., New York (1953).

22. Roderick, W.R., J. Chem. Ed., 43, 510 (1966).

23. Baker, R.A., J. Water Pollution Control Federation, 34, 582 (1962).

24. Rosen, A.A., R.T. Skeel, and M.B. Ettinger, J. Water Pollution Control Federation, 35, 777 (1963).

25. Rosen, A.A., J.B. Peter, and F.M. Middleton, J. Water Pollution Control Federation, 34, 7 (1962).

26. Spaulding, J. Am. Water Works Ass., 34, 277 (1942).

27. Baker, R.A., J. Water Pollution Control Federation, 34, 582 (1962)

IX. ANALYSIS FOR ORGANIC POLLUTANTS

A. Nonspecific Analyses

The chemical oxygen demand (COD) is widely used as a measure of the organic pollutional load of a water or waste water. It is based on the principle that most organic compounds are oxidized to CO_2 and H_2O by strong oxidizing agents under acid conditions. What the measurement represents is that amount of oxygen that would be required from a receiving water if oxygen alone could oxidize the organic material to the same end products in the absence of microorganisms; or the oxygen that would be needed for aerobic microbial oxidation to CO_2 and H_2O assuming that the organics are biodegradable. The method determines total oxidizable organics but is not capable of distinguishing between those that are biodegradable and those that are not.

Furthermore, the COD test gives no indication of the rate at which organics would be oxidized in a stream. For these reasons, it is dangerous to generally attempt correlation between COD and BOD values although a relation may be established empirically for a given waste.

The test involves reacting a standard dichromate aliquot in acid solution with a sample containing organic matter until oxidation is complete. Excess dichromate is measured by titration with freshly standardized ferrous ammonium sulfate using Ferroin indicator.

$$14H^+ + Cr_2O_7^= + 6Fe^{++} = 2Cr^{+3} + 6Fe^{+3} + 7H_2O \qquad \text{IX-1}$$

Any substance that will reduce $Cr_2O_7^=$ will interfere with the COD procedure leading to high results and the principal interference is chloride ion.

$$Cr_2O_7^= + 6Cl^- = 2Cr^{+3} + 3Cl_2 \qquad \text{IX-2}$$

This difficulty may be overcome by the addition of $HgSO_4$ to samples before refluxing to tie up chloride ion as a soluble mercuric chloride complex or by applying a correction of 0.23 x mg/l Cl^- to the analytical result. The latter correction derives from the stoichiometry of the above interference reaction.

The Total Carbon Analyzer allows a total soluble carbon analysis to be made directly upon an aqueous sample. The result is obtained within a matter of minutes and the method required less than 0.5 ml of sample. This volume includes several rinsings of the injection syringe as the actual sample volume required is only 20 µl. If particulate matter is excluded the test represents total soluble carbon and if inorganic carbon is excluded or corrected for, the results represent dissolved organic carbon (DOC).

The aqueous sample is injected directly into a combustion tube, heated to 970°C in a constant flow of oxygen gas. Any organic matter is oxidized completely to CO_2 and water vapor on an asbestos packing impregnated with catalyst and these are carried from the combustion tube by the oxygen stream.

Outside the combustion tube, the water is condensed and the CO_2 is swept through a continuous flow sample cell in a nondispersive infrared CO_2 analyzer. The instrument signal recorded on a linear strip chart recorder and the peak height or peak area is proportional to the concentration of carbon in the aqueous solution.

A standard curve is established over the concentration range of interest by adjusting the amplifier gain to give mid-scale response for the mid-concentration standard, and plotting peak height or peak area versus concentration. Comercial instruments are capable of reproducible readings at the 1-2 mg/l carbon level. Peak height for any given carbon concentration is relatively independent of furnace temperature above 940°C and the same stability is exhibited over a wide range of oxygen flow rates. Standards may be any carbon compound of known purity; Na_2CO_3, potassium acid phthalate (KHP), trishydroxymethylaminomethane (THAM), glucose or benzoic acid. Literature reports (1,2,3,4) are in general agreement that the overall precision is in the order of ±2%.

Inorganic carbon can be removed prior to analysis by acidification and sparging which does not remove volatile acids such as

formic and acetic acids (3). Alternatively, a diffusion cell containing a trough of KOH may be used to trap liberated CO_2 from acidified samples just prior to withdrawing a liquid sample for carbon analysis.

Biochemical oxygen demand (BOD) is the quantity of oxygen required by a biological community over a period of time to meet its respiratory demands. In this process, reduced organic compounds are oxidized by microorganisms releasing energy for use in synthesis of cellular material which results in population growth. The general equation for aerobic respiration using glucose is:

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O + \text{energy} \qquad (IX-3)$$

For waters with relatively large quantities of organic matter, bacterial metabolism will account for most of the oxygen consumed. But in most natural waters, algae also contribute to the BOD, either by their own cellular respiration or as degradable organic matter as well as the rate at which that degradation will occur.

The curve of BOD in organic waste water plotted against time initially has a steep slope but gradually decreases until a plateau is reached as the demand is satisfied. This relation can be described by the following equation:

$$y = L(1 - 10^{-K_1 t}) \qquad (IX-4)$$

where y is the BOD at time t, L is the ultimate demand when oxidation is complete, K_1 is the rate constant, and t is the time interval after oxidation has begun.

The oxygen depletion curve is then a result of organic matter oxidation by bacteria. The resulting growth of the bacterial population is described as logistic or "S" shaped curve with the equation:

$$N_t = N_0 e^{-Kt} \qquad (IX-5)$$

where N_0 is the initial number of cells, N_t is the number of cells after time t, e is the base of natural logarithms, and K is the growth constant.

The rate constant for growth or BOD is affected by environmental factors such as substrate concentration, inorganic nutrient concentration, pH, temperature, toxic compounds and kinds of microorganisms. Thus, although BOD describes the rate of organic matter oxidation under a given set of conditions, the measure of biodegradable organic matter is subject to factors which can result in wide variations in values. To control part of this variability, the BOD measurement is standardized to a considerable extent by holding time, temperature and dilution water constant. But in order to adequately determine the BOD rate for a given waste or receiving water, reasonably long-term studies are needed in order to quantify the variables in the BOD equation.

Routine measurements of BOD include initial and final dissolved oxygen determination with either an oxygen sensitive electrode or by the Winkler titration procedure, over a 5-day period at 20°C. If the sample contains no microorganisms (industrial wastes) seeding with small volumes of sewage may be required. BOD is then calculated as mg/l of oxygen consumed by the sample under these conditions.

B. Separation and Identification of Organic Pollutants

In this section, we will focus our attention on selected gas-liquid and thin layer chromatographic procedures for the detection of specific types of pollutants (pesticides and phenols) as well as compounds of interest in the control of biological sewage treatment processes (digester gas, volatile and fatty acids).

B.1. Application of GLC to Pesticide Analysis

Gas chromatography has been extensively used in the identification and analysis of pesticides in ground, surface and potable waters as well as in sediments, organic tissues and bottom muds. Although the flame ionization, electron capture and microcoulometric

detectors employed for pesticide analysis are quite sensitive, direct aqueous measurement is usually not feasible due to the variety of interfering substances which occur in natural or polluted waters. Furthermore, quantities of sample larger than the detection limits of the detectors are often required for confirming spectral data.

Liquid-liquid extraction procedures are preferable to carbon adsorption for sample pre-concentration (5). Choices of solvents vary as shown in Table IX-1 for several organo-phospherous pesticides. Chloroform and ether appear to be preferred solvents for the phenoxyalkyl acids with extractions performed at pH 2.0. Recoveries range from 93-102% (5,6,7). Neutral pH values generally are optimum for the extraction of chlorinated hydrocarbons.

After extraction clean-up procedures employing column partition chromatography are necessary. Silica gel columns are most effective for chlorinated hydrocarbons and florisil columns are used for organo phosphorous pesticides with elution performed with a variety of non-polar solvents (8). Column, temperature and detector conditions for the separation of three classes of pesticides are summarized in Table IX-2. Additional column data are available in the literature (8,9).

Retention data are seldom sufficient for the confirmation of pesticide identity. Faust and Suffet (8) have recommended the use of a flow stream splitter prior to flame ionization detection to absorb organophosphorous components on KBr. With this procedure it is relatively easy to correlate retention data with confirming spectral data. Infra-red spectra may be run on the KBr pellets directly and ethanol elution of the pellets results in a solution ready for ultraviolet analysis.

B.2. Application of GLC to Phenol Analysis

Adequate separation and resolution of phenols and phenolic acid derivatives are extremely difficult at reasonable operating temperatures due to the activity of these functional groups. Direct aqueous injection is possible and the techniques and column operating conditions for this analysis have recently been reviewed (10). Acid washing of diatomite supports does not seem to affect phenol

Table IX-1. SOLVENT EXTRACTION OF ORGANOPHOSPHOROUS PESTICIDES (1)

Pesticide	Solvent	No. of Extractions	pH	Mean Recovery %
Parathion	1:1 hexane and benzene	Continuous	--	97
Parathion	benzene	1	acid	99-100
Malathion	dichloromethane	3	7.0-8.0	100?
Abate	Chloroform	3	1.0	70
Dipterex and DDVP	ethyl acetate	2	8.0	94.5

Table IX-2. SUMMARY OF SEPARATION CONDITIONS FOR PESTICIDES WITH GLC

	Column Packing	Column Length (ft)	Temp. °C	Detector
Chlorinated Hydrocarbons	5% DC-200 oil on 60/80 Chromosorb P	6	195	MC
	3% SE 30 on 80/90 Anakrom ABS	4	195	EC
	3% Apiezon L grease on 80/100 Chromosorb W/HMDS	3 or 4	190 or 200	EC
Organophosphates				
	5% DC-200 oil on 60/80 Chromosorb P	6	195	MC
	3% SE-30 on 80/90 Anakrom ABS	4	195	EC
	5% Dow-11 on 60/80 Chromosorb W	6	270	FID
Phenoxyalkyl Acids and Esters				
	5% silicone on 80/100 Chromosorb W	6	200	EC
	5% Dow-200 oil on 60/80 Chromosorb W	5	TP; 200-230	MC

Table IX-3. COLUMN CONDITIONS FOR PHENOL ANALYSIS'

	Column Condition	Reference
phenols from tall oil	Apiezon E, propylene glycol on silica	6
phenols and cresols	Nylon 66 and 50 HB 2000 on Firebrick	7
wood phenols	20% Carbowax 20 M on diatomaceous earth	8
t-butyl phenol mixtures	Silicone oil 550 (3 pts), Carbowax 4000 (2 pts) on Chromosorb W - 220°C	9

analyses by GLC and silanization of the support leads to increased peak tailing and decreased sensitivity for direct aqueous injection techniques. Carbowax 20M and FFAP (varian aerograph, polyester type free fatty acid phase) in the 5-10% loading range appear to be the best liquid coatings although many substrates will separate and permit quantification of selected monohydric phenols. The combination of FFAP on Chromosorb T provides maximum separation, highest sensitivity and symmetrical peaks with minimum tailing.

Although supplemental identification by spectrophotometric or other chromatographic procedures is necessary for complex mixtures, simple phenols may be handled adequately with flame ionization dilution down to 1.0 mg/l without preliminary sample concentration.

Satisfactory results can be obtained by converting phenols and phenolic acids to trimethylsilyl ethers and esters prior to GLC separation to greatly increase volatility, thus allowing operation at much lower temperatures (130-160°C). The dried residue from the solvent extraction step is mixed with a small volume (1.0-5.0 ml) of BSA [N, O - Bis - (Trimethylsilyl) - Acetamide]. After allowing time for the completion of the silylation reaction (10-20 min) the liquid produce may be directly injected into a chromatograph. Excellent resolution can be obtained on 3 foot columns of SE 30 silicone gum (10%) on acid washed chromosorb W at 140°C. Order of elution under these conditions is: phenol < methylphenols < benzoic acid < methoxyl phenol < dihydroxylphenols = methylated acids < methoxylated acids < monchydroxy acids < polyhydroxy acids, in order of increasing retention times.

B.3. Application of GLC to Volatile Acid and Digester Gas Analysis

Gas chromatographic analysis of volatile acids is approximately an order of magnitude more sensitive than older methods involving liquid column partition or paper chromatographic techniques. Most workers (11,12,13) recommend a Carbowax 20M and H_3PO_4 column; although the column compositions vary 8% Carbowax 20M and 2% H_3PO_4 are probably best. Direct aqueous injection may be employed with a flame ionization detector. The procedure is subject to "ghosting" and often peak areas must be used for quantitative work as peak

heights are not linear with concentration. Intermittent water injections may be required to eliminate ghosting and although 3 foot columns have been employed longer columns may be desirable. Recent work (93) using Carbowax 20M treated with Tergitol E-68, temperature programming and a carrier gas stream wetted by passing through a $CuSO_4 \cdot 5H_2O$ precolumn has resulted in excellent resolution of all volatile acids (acetic through octanoic) of common interest. With the exception of acetic acid this procedure gives reliable results down to 6.0 mg/l.

Higher fatty acids in sludge samples may be resolved using diethyleneglycol succinate (DEGS), 10% on 60-80 mesh Chromosorb W. A sample is extracted with ether, dried, and the residue converted to the methyl ester by heating in MeOH and 10% MCl for 2.0 hours. After pH adjustment, the esters are re-extracted into ether and injected directly into the chromatograph at 180°C. Lauric, myristic, palmitic and other fatty acids can easily be detected down to 1-5 mg/l.

The volume percent composition of CH_4, CO_2 and H_2S in sludge digester gas may be determined on columns of silicone grease (28%) on 28-48 mesh C-22 firebrick 70 ft. in length (10). Thermal conductivity detection is adequate and column temperature is maintained at 30°C. If hydrogen in the gas sample (not separated by silicone column) does not exceed 5 vol. %, the percentage of each gas present is directly related to the relative ratio of sample peak area to total peak areas.

B.4. Application of TLC to Phenol Analysis

Thin layer chromatography may be the fastest method available for qualitative detection of phenols in water or waste water. As with pesticide analysis, liquid-liquid extraction or freeze concentration should be employed for sample pre-concentration. Elution from the plates in Ethanol after development is necessary for spectral confirmation.

B.4.a. Plate Preparation

A slurry containing 5 gm Silica Gel to 10 ml water can be pre-

pared in a mortar and poured onto the glass plates that have been lined on all edges with strips of masking tape. Spreading of the layer is accomplished by rolling in one direction with a glass rod (0.5 cm diameter). After drying at room temperature for 15 minutes, the plates can be oven dried at 100°C for 30 minutes, cooled and stored in a dessicator until use.

Uniformity of thickness on any one plate can be obtained remarkably well with a little practice, however, thickness will vary from plate to plate.

Maximum uniformity in thickness of the static phase can be obtained with the use of any of several mechanical applicators that are commercially available.

B.4.b. Application of Sample

Most phenols and phenolic acids are soluble in volatile organic solvents such as ethyl ether or 95% ethanol. Generally, the more volatile the solvent the smaller the spot size after application will be. A gentle stream of dry air directed onto the plate greatly facilitates the application of sample.

Proximity of spots on the same plate is a function of sample concentration, but a minimum horizontal separation of 2.5 cm was found to be adequate in our study. All spots were placed 1-2 cm above the solvent reservoir to prevent draining during development.

B.4.c. Development

B.4.c.i. Developing Chamber

Almost any ordinary vessel can be used; one gallon jars, drinking glasses, or commercially available containers of different sizes covered with plastic caps, glass plates or Saran Wrap. Solvent can be placed in the vessel which is then capped so that an approach may be made to air saturation with solvent vapor. Plates containing the sample plus known standard compounds can then be rapidly inserted for development. R_f values will vary from run to run using this procedure although $R_{standard}$ values are

reasonably reproducible.

If reproducible R_f values are desired, constant temperature and air saturation with the solvent system must be provided. A simple means of accomplishing this is to cap the chamber with a two-hole stopper fitted with a stop cork and a separatory funnel with the tip bent to touch the inside of the chamber. A prepared plate with the bottom 3.0 cm free of Silica Gel can be placed in the chamber which contains solvent standing to a depth of 1.5 cm. After air saturation is obtained, solvent can be run in from the separatory funnel to begin development

B.4.c.ii. Solvent Systems

1.	Ethyl ether	---	
2.	Benzene/ethanol	98/2;95/5;90/10	vol/vol
3.	Benzene/methanol/acetic acid	95/8/4	vol/vol
4.	Benzene/dioxane/acetic acid	90/25/4	vol/vol
5.	Benzene/acetic acid/water	125/72/3	vol/vol
6.	Isopropanol/ammonium hydroxide/water	200/10/20	vol/vol

B.4.d. Detection

B.4.d.i. Drying

Plates can usually be air dried in 5-10 minutes except in cases where acid-base indicators are to be sprayed and the solvent contains an acidic or basic component. In the latter cases oven drying may be needed.

B.4.d.ii. Fluorescence

Dried plates should be observed before spraying for any visible fluorescence under a UV hand lamp. Many of the phenolic acids fluoresce brillantly and their location can be marked with small indentations in the Silica Gel surface. In some cases, exposure to NH_3 fumes greatly enhances fluorescence.

B.4.d.iii. Chromogenic Reagents

Spraying must be done carefully to prevent draining of the Silica Gel. Sometimes oven heating enhances color formation and in other cases the fading or changing of a color with time may be indicative of certain compounds. The chromogenic reagents and the structural implications inferred from them are listed in Table IX-4.

Table IX-4. USEFUL CHROMATOGRAPHIC SPRAYS FOR THE IDENTIFICATION OF PHENOLIC COMPOUNDS

Spray		Structural Implication
1. Ferric chloride-ferric cyanide spray: 3% $FeCl_3$ in water followed by 3% $K_3Fe(CN)_6$		Phenols in general, particularly those of catechol-pyrogallol type.
2. 2,4-dinitrophenylhydrazine 0.1% in 2N HCl		Aldehydes and ketones
3. Diazotized p-nitraniline		
a. p-nitraniline, 0.3% in 8% HCl	50 ml	Phenols in general, particularly mono-hydroxy phenolic compounds.
b. $NaNO_2$, 5% in water	3 ml	
c. Na_2CO_3, 10% in water	50 ml	
4. Tetrazotized benzidine		
a. Benzidine solution 5 gr. dissolved in 14 ml conc. HCl and diluted to 1 liter	1 volume	Phenols in general, particularly those of resorcinol-phloroglucinol type.
b. Aqueous 10% sodium nitrate	1 volume	
5. Vanillin Reagent		Phloroglucinol-resorcinol phenols not having carbonyl or carboxylic acid groups on the ring or conjugated with it.
a. Vanillin, 10% in 95% ethanol	2 volume	
b. Conc. HCl	1 volume	

C. Ultraviolet and Infrared Identification

There are relatively few instances reported in the literature in which UV spectrophotometry has been applied directly to natural or polluted waters with effective results. Naturally colored waters show only end absorption with the cutoff wavelength dependent only on path length (15). Absorption due to natural color bodies in the 200-350 mμ range is strongly affected by pH, increasing as pH increases. Some workers (16) have shown that absorption at 220 mμ is linearly related to COD values. In all such applications, the nature of the organic compounds was unknown.

Ultraviolet and infrared spectrophotometric techniques are most often employed to obtain final confirmation of the structure of a component of a polluted sample only after concentration, separation and cleanup procedures have been performed.

C.1. Identification of Pesticides

Spectrophotometric confirmation of pesticide structure is possible by trapping peaks (split stream) in freeze traps, gas tubes or adsorption on pellets of KBr. In many cases spectra on the eluted fractions in the gas phase from GLC separations are most useful since fine structure is apparent on such spectral traces at low scan speeds. In cases where a component (or fraction) must be handled as a solute in an organic solvent attention must be given to the absorption characteristics of the solvent. If measurements are made versus air the solvent cutoff must be known, and if measurements are made versus solvent (usually preferable) wide slit widths may result in poor wavelength resolution in regions of solvent absorption.

Qualitative analysis consists of matching the spectra of a suspected component with that of a known pure sample or comparing the wavelength positions and intensities of absorption of the component with data listed in several standard reference texts (17,18,19).

Many of the major IR absorption bands of the organophosphorous pesticides are well documented (20). A major difference between a parent pesticide and its oxidation product (oxon) is the P=O free band

of the oxon at 7.9 μ as shown in Table IX-5. In general, microgram quantities are required for IR examination whereas nanogram quantities are sufficient for UV examination (Table IX-6).

Table IX-5. CHARACTERISTIC IR ABSORPTION OF ORGANOPHOSPHORUS PESTICIDES

Group	Wavelength (μ)	Intensity*
P = O free	7.9	m
P-O-C aromatic	8.1	m
P-O-C aliphatic	9.7-9.8	s
P-O-ethyl	8.6	w
P-O-methyl	8.4	w
P = S	12-13	m
C-NO_2 aromatic	7.4	s
C = O	5.7-5.9	s

* m = medium; s = strong; w = weak

Table IX-6. ULTRAVIOLET ABSORPTION MAXIMA AND LIMITS OF DETECTION FOR SELECTED PESTICIDES (7)

Compound	λ_{max}	Detection Limit (ng)+
Diazinon	247.5	210
Parathion	274	90
Baytex	252	69
p - nitrophenol	231,313	39
Paraoxon	271	--
Bayoxon	248.5	58

+ Determined in 60 μl microcell

C.2. Identification of Phenols

Phenolic degradation products of water borne natural polymers have been characterized by UV spectrophotometry (21,27). Substituted phenols display sufficiently different UV absorption characteristics to permit identification as shown in Table IX-7. Bathochromic shifts resulting from base addition to alcoholic solvents are particularly useful for confirming substitution patterns after elution with ethanol from thin layer plates.

Table IX-7. UV ABSORPTION CHARACTERISTICS OF SELECTED PHENOLS (7)

Compound	Absorption Maxima, mμ E+OH	E+OH - NaOH
O-dihydroxybenzene	203,219,279	262,290
m-dihydroxybenzene	205,223,277 283	245,295
3-methoxy-4-hydroxy-benznedehyde	210,255,320	250,350
3-methoxy-4-hydroxy-benzoic acid	259,293	300
3,4-dihydroxybenzoic acid	208,252,292	277,302

REFERENCES

1) R. A. Minear. M.S. Thesis, University of Washington (1966).

2) C. E. VanHall, J. Safranko and V. A. Stenger. Anal. Chem. 35, 315 (1963).

3) C. E. VanHall, D. Barth and V. A. Stenger. Anal. Chem. 37, 769 (1965).

4) R. B. Schaffer, et al. Jour. Water Poll. Control Fed., 37, 1545 (1965).

5) K. Erne. Acta Chem. Scand., 17, 1663 (1963).

6) D. C. Abbott, et al, Analyst, 89, 480 (1964).

7) O. M. Aly and S. D. Faust. Jour. Amer. Water Works Assoc., 55, 639 (1963).

8) S. D. Faust and I. H. Suffet. Analysis for Organic Pesticides in Aquatic Environments. Microorganic Matter in Water, ASTM STP 448, American Society for Testing and Materials (1969).

9) T. R. Lynn, C. L. Hoffman and M. M. Austin. Guide to Stationary Phases for Gas Chromatography. Analabs, Inc., Hamden, Connecticut (1968).

10) R. A. Baker and B. A. Malo. Environmental Sci. and Tech., 1, 12, 997 (1967).

11) J. F. Andrews, J. F. Thomas and E. A. Pearson. Water and Sewage Works, III, 4, 206 (1964).

12) E. Hindin, et al. ibid., III, 2, 92 (1964).

13) J. W. Sugar and R. A. Conway. Journal Water Pollution Control Assoc., 40, 9, 1622 (1968).

14) Standard Methods for the Examination of Water and Waste Water APHA, AWWA, WPCF, 12th Edition (1965), p. 535.

15) A. P. Black and R. F. Christman. Jour. Amer. Water Works Assoc.

16) T. Hanya and N. Ogura. Adv. Org. Geochem., Proceedings of the International Meeting, Milan 1962. Pergaman Press (1964).

17) J. P. Phillips. Spectra-Structure Correlation, Academic Press New York (1964).

18) C. N. R. Rao. Ultraviolet and Visible Spectroscopy. Butterworths, London (1961).

19) L. J. Bellamy. The Infrared Spectra of Complex Molecules. John Wiley & Sons, New York, 2nd Ed. (1957).

20) N. T. Crosby and E. Q. Laws. Analyst, 89, 319 (1964).

21) R. F. Christman. Environmental Science and Technology, 1, 4, 303 (1967).

22) R. F. Christman and M. Ghassemi. Jour. Amer. Water Works Assoc., 58, 6, 723 (1966).

X. ANALYSIS FOR METAL POLLUTANTS

A. Physicochemical characteristics of metal ions in aquatic environment

This discussion will be concerned with the nature of the interaction between a metal ion and its aqueous environment, particularly so as to consider the possible states of the metals as related to the possible methods of analysis. The purpose is not to consider all the sources, transport, controls on and incidences of metal species in the natural water environment; however, some principles of the controlling mechanisms will be considered.

In aqueous solutions of electrolytes there are electrostatic interactions among the charged species which affect the free energy of the ions and, therefore, their chemical activity. In many methods of analysis, such as atomic and molecular absorption spectrophotometry, emission spectroscopy and activation analysis, the detection process is a stoichiometric one in that the signal obtained is directly related to the number of atoms or ions being measured. In other methods, however, particularly electrochemical analyses, the chemical activity, a, is being measured. It is related to the concentration, C, through the equation

$$a_i = f_i \times C_i \qquad \text{(X-1)}$$

where f_i is the activity coefficient and activity and concentration each have the units of moles per liter.

The principal factor affecting the activity coefficient is the ionic strength, I, also expressable as moles per liter, which is a measure of the total concentration of charged species and is defined as

$$I = 1/2 \; \Sigma C_i \; z_i^2 \qquad \text{(X-2)}$$

where z_i is the charge on ion i. Examples of values of ionic strength

are 3.7×10^{-3}M for a typical municipal water, 7.7×10^{-3}M for the Ohio River, and 0.7M for sea water (1). The effect of ionic strength on the activity coefficient may be expressed through the Davies equation at 25°C

$$- \log f_i = 0.509 \times z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2\ I \right) \qquad X\text{-}3)$$

Thus the single ion activity coefficient varies both with ion charge and ionic strength. As the ionic strength approaches zero, the activity coefficient approaches unity. Examples of activity coefficients are, for a municipal water with $I = 3.7 \times 10^{-3}$M, $f_i = 0.94$ for univalent ions and 0.77 for divalent ions; for sea water with I = 0.72M, $f_i = 0.7$ for univalent ions and 0.25 for divalent ions. Thus, in using activity measurements to determine the concentrations of charged species, activity coefficient corrections are frequently necessary.

Another important phenomenon affecting the state of metal ions is their ability to form hydroxo complexes. Thus, for example, iron(III) can exist in aqueous solution as a "bare" Ve^{+++} ion, but also as $Fe(OH)^{++}$, $Fe(OH)_2^{+}$, $Fe(OH)_4^{-}$ and even dimers and polymers such as $Fe_2(OH)_2^{+4}$(8). The sole factor affecting the relative concentration of these monomeric species is pH. Thus at pH of 2 or less, the predominant species is Fe^{+++}, at pH 4 $Fe(OH)^{++}$, at pH 6 $Fe(OH)_2^{+}$, and at pH 8 and higher $Fe(OH)_4^{-}$. All of these various hydroxo complexes of iron are in mutual equilibrium, even though only one species may predominate at a given pH. One important effect they have is on the solubility of iron(III). Thus as the pH is increased, the solubility of $Fe(OH)_3$ will generally be much higher than if such complexes were not formed.

A second important effect of this type of complex formation concerns the optimum condition for an analysis. If the spectrum of an organic complex of iron(III) is the basis of the analysis, it is frequently necessary to adjust the pH so as to reduce the competition of OH^- ions for the iron(III). The same applies in using a chelate for iron in order to extract it with an organic

solvent prior to analysis. Also when an ion selective electrode is being used to measure the activity of an ion in solution, such as the divalent ion electrode for Fe(II), it will detect the Fe^{++} form. If some of the Fe(II) is in other soluble states, such as hydroxo complexes, that portion will not be detected. Generally, the higher the oxidation state of a metal, the more readily it forms hydroxo and other complexes. Thus, these are not usually important phenomena for the alkali metal ions.

A great variety of other metal ion complexes can form in natural and treated waters Aluminum is readily complexed by fluoride to form such species as AlF^{++}; iron(II) also forms complexes with fluoride. Tannin, which is an aromatic carboxylic acid, a weak acid with a pH of between 5 and 6; it has been shown that tannic acid forms a relatively strong complex with Fe^{++} (12). In measurements of the calcium activity in sea water, it was shown that approximately 16% of the calcium is not ionized, but is complexed or bound as ion pairs (27); similarly, it was shown that 10% of the magnesium is bound, probably by sulfate, carbonate and bicarbonate (26).

Ion pair formation can occur in relatively concentrated solutions and can be considered as another kind of metal complex. Thus, for example, the interaction of Ca^{++} and HCO_3^- to form $CaHCO_3^-$ or soluble $CaCO_3$ is essentially ion pair formation. In a typical municipal water, it has been calculated that perhaps only 0.1% of the calcium forms the ion pair $CaCO_3$; similar 1.5% may form $CaSO_4$ (1). Even univalent cations can form ion pairs, such as $NaSO_4^-$ and KSO_4^- (10). Just as in the case of hydroxo complexes of metals as well as influence their ability to be detected by other means, as well as separated or concentrated to facilitate analysis.

Another important state of metals in water is the colloidal form. Thus, many crystalline or amorphous metal hydroxide, carbonate, silicate, and other species, as well as inorganic polymers can exist in the colloidal state and remain relatively stable for long periods of time. In addition, soluble monomeric metal ions can adsorb onto the surface and thereby be associated with other colloidal species. All of these colloidal forms of metals can be significant sources of their total analyzable concentration. They

will not settle out from solution unless coagulated; they may, however, be removed with fine filters in order to distinguish them from truly soluble species. However, it may require several hours of digestion in concentrated acid to convert them to a soluble and, hence, analyzable state.

A final important variable affecting the state of a metal ion species is the redox potential of the solution. Thus, for the reduction reaction

$$Fe^{+3} + 1\ e \leftrightarrow Fe^{++} \qquad (X\text{-}4)$$

the equilibrium activity ratio between these two iron species is determined by the reduction (redox) potential of the solution, Eh, the "h" referring to the fact that this is the potential compared to the normal hydrogen potential taken as zero. The equilibrium relationship at 25°C is

$$Eh = E^\circ - 0.059 \log \frac{(Fe^{++})}{(Fe^{+3})} \qquad (X\text{-}5)$$

with E° as the standard reduction potential for this reaction in volts, and ( ) refers to ionic activities. This Nernst equation indicates that the more positive Eh is, the smaller is the ratio of $(Fe^{++})/(Fe^{+3})$, provided that the system is at equilibrium. Generally, the reduction potential of natural waters increases with oxygen concentration, in which case, the Fe^{+3} should increase as well.

There are two principal difficulties in utilizing this concept and relating it to the behavior in natural waters (19). First, it is difficult to measure reduction potentials; and second, there is no assurance, once an accurate measurement is made, that the redox system of interest is in equilibrium with it. Nevertheless, the fact that two or more oxidation states can exist for the same metal can have a profound effect on the chemical analysis of that

metal. Generally, the chemical behavior of the various oxidation states is quite different, including their solubilities and ability to be complexed and chelated, extracted and precipitated; also their molecular absorption spectra are different. To simplify the measurement of the total concentration of such a species, it is usually convenient to convert all forms into one oxidation state.

It is apparent from the above discussion that the physicochemical state of a metal ion can have a great effect on almost every analytical process, with the possible exception of the measurement of radioactive species. Keeping this point in mind, the discussion will not turn to a brief survey of the sommon instrumental techniques for metal analysis in aqueous systems.

B. Molecular absorption photometry and colorimetry

The most widely used techniques for the analysis of metals in water, other than the alkali and alkaline earth metals, involve the absorption of light by the metals in the form of soluble complexes, chelates, compounds, or "lakes". Although many of these metals at high concentrations do absorb light, at the levels to be found in environmental, municipal, industrial and waste waters, it is necessary to form a more highly light adsorbing species, (to use a "color developing agent"), which presumably and optimally is specific for the test metal of interest.

Many of these current techniques for metals involve species which adsorb visible light. Table X-1 lists such methods for thirteen metals, showing the minimum detectable amounts and some important interferences. The optimum wave length in each case is in the visual colorimetry and instrumental measurement, such as filter photometers and spectrophotometers.

One of the principal advantages of the use of such color developing agents resulting in light absorption in the visual region is the fact that visual colorimetry can be utilized and it is not necessary to resort to instrumental detectors. However, usually the use of a spectrophotometer can improve the sensitivity and accuracy of the method. One of the principal disadvantages of many of these techniques is that there are many interferences which re-

Table X-1. METAL IONS DETERMINED BY COLORIMETRY AND MOLECULAR ABSORPTION SPECTROPHOTOMETRY *

Metal	Color Developing Agent	Optimum Wave Length	Minimum Detectable Conc.	Possible Interferences
		mu	µg/l	
Al	"aluminon"	525	2	F, Ca, chlorine, sulfite polyphosphate
As	diethyldithio-carbamate	535	1 µg	Co, Ni, Hg, Ag, Pt, Cu, Cr, Mo, Sb
B	curcumin	540	0.2 µg	nitrate
Cd	dithizone	518	0.5 µg	Pb, An, Cu
Cu	cuprethol	435	0.02 (visual)	Bi, Hg, Co, Ni, Ag, etc.
Cr	diphenylcarbazide	540	10	V, Fe, Mo, Cu, Hg
Fe	Phenanthroline	510	3 µg	Cr, Zn, Co, Cu, Ni, etc. oxidants
Pb	dithizone	510	2 µg	Heavy metals, organics
Mn	persulfate	525	5 µg	Br, I
Ni	Heptoxime	445	---	---
Se	diaminobenzidine	420	1 µg	Fe, I, Br, oxidants
Ag	dithizone	462 620	0.2 µg	Fe, Cl_2, oxidants
Zn	dithizone	535	---	Cd, Cu, Pb, Ni

* "Standard Methods for the Examination of Water and Waste Water," 12th Edition, American Public Health Association, New York, 1965.

quire, in some cases, a high degree of chemical sophistication and intuition to eliminate. An alternative approach is to resort to more expensive instrumental detectors, such as stomic absorption and emission spectroscopy, where the interferences may be substantially fewer.

Aside from relying on chemical means or pre-separating techniques, such as ion exchange chromatography, to reduce interferences, in some cases, when the interference is due to overlap of absorption spectra, it is possible, using spectrophotometry, to correct for such overlap, thereby removing the interference. An example of such a method is the analysis of nickel in industrial water, using the yellow-green complex of nickel with diethyldithiocarbamate (6). Copper, cobalt and bismuth also form complexes with the latter which absorb light at 328 mμ, and corrections must and can be made by determining their concentrations separately. If copper is the sole interfering metal, two measurements can be made on the unknown sample, one at 328 mμ, the absorption maximum for the nickel complex, and one at 436 mμ, that of copper. The two measurements are required because each of these respective complexes adsorbs light to some extent at the absorption peak of the other. After measuring the absorbance of standards, containing known mixtures of copper and nickel, at these two wave lengths, the concentrations of copper and nickel separately may be calculated from the two measurements on the mixture of the test solution, simply by solving two simultaneous equations.

Although many of these colorimetric and photometric techniques have been used for many years and may require relatively inexpensive or virtually no instrumentations, in some cases, they are as accurate, precise and sensitive as such techniques as emission spectroscopy, atomic absorption spectrophotometry and neutron activation analysis, which require relatively expensive instrumentation.

C. Atomic Absorption Spectrophotometry

Atomic absorption spectrophotometry (AAS) has wide application in the analysis of metal ions in natural and treated waters, as well as waste effluents because of its speed, low cost per analysis,

simplicity, and frequent ability to analyze complex mixtures without prior separation. A wide variety of applications have been reported, including analyses of industrial water and waste water (4,20), fresh water (9), sea water (15,5), and sewage (25).

The sensitivity of atomic absorption is generally considered that concentration of test species that produces one percent absorption of the appropriate wave length passed through the flame into which the test solution is being aspirated (16). One definition of detection limit is that concentration giving a detection signal twice the variability of the background. In natural waters, many metals can frequently be analyzed directly, since they are present at sufficiently high concentration so as to exceed the sensitivity limit; for example, sodium, potassium, calcium, magnesium, strontium, lithium, manganese, copper and zinc (9). In other cases, AAS is not sensitive enough and preconcentration and solvent extraction is required, such as for copper, lead, zinc, nickel, iron and cadmium in industrial waters (4,20); cobalt, nickel and lead in fresh natural waters (9); and iron and nickel in brine (15).

Several preconcentration techniques have been utilized for the analysis of metals in water, including coprecipitation, ion exchange and solvent extraction. The advantage of the latter is that, in addition to concentrating the metal, the inherent sensitivity of AAS for many metals in an organic solvent is higher than in water. For example, one study has indicated that the sensitivity in methyl isobutylketone (MIBK), a common solvent used for this purpose, compared to water was greater for metals in the range of 0.25 to 1.0 mg/l by the following factors: Fe 3.8, Cu 4.6, Pb 6.3, Zn 3.0, Cd 2.6 (20).

The limits of detection for several metals in water with one instrument are shown in Table X-2, along with a comparison for the similar limits obtained when the metals are first chelated in water, using a chelating agent such as sodium diethyldithiocarbamate, followed by extraction with MIBK. This method can frequently improve the sensitivity by a factor of as much as 50. In one of the studies of chelation and extraction prior to AAS analysis, it was found that the proper choice of chelating agent prior to extraction could in-

crease the sensitivity, e.g. oxime for iron and dimethylglyoxime for nickel; also that the presence of salt in brine reduces the sensitivity by a factor of 2 (15).

Table X-2. COMPARISON OF DETECTION LIMITS FOR SEVERAL METALS WITH ATOMIC ABSORPTION SPECTROPHOTOMETRY. DIRECTLY IN WATER AND USING SOLVENT EXTRACTION

	Detection Limits (µg/l)			
		Solvent Extraction		
Metal	Direct in H_2O (16)	Ref. (20)	Ref. (9)	Ref. (15)
Fe	5	2-3		0.2
Cu	5	0.2		
Zn	2	0.3		
Pb	30	5	0.8	
Cd	1	0.7		
Co	5		0.4	
Ni	5		0.4	1.0

The state of the metal ion in solution can sometimes reduce the ability of AAS to detect it, as can the presence of other species in solution. Such interferences can generally be classified as "chemical", "ionization", and "matrix" (16). A chemical interference can occur when a compound of the test element is formed in the flame and this element does not dissociate. One example is the interference of silicon with a strontium analysis; the addition of lanthanum binds the silicon, freeing the calcium. Ionization interferences result when the element in the flame is ionized, adsorbing a different wave length; this can be reduced by flame adjustment. The presence of large amounts of dissolved solids can reduce the light

adsorption, a matrix interference, essentially due to a reduction in solution flow through the burner; thus, high phosphates of the order of 1.0M can reduce the signal in copper and magnesium analysis by 20% (16). Finally, it should be noted that undissolved particulates, such as iron oxide, will generally not contribute to light absorption. Thus, if one wished to determine total iron in a sample, the particulate iron should first be dissolved prior to AAS analysis (20).

D. Ion Selective Electrodes

Ion selective electrodes operate on a principle similar to that of the glass electrode for the measurement of pH. Their theory and applications for water analysis have been recently reviewed (1). They are commercially available to measure a wide variety of cations and anions, including the alkali metals, calcium, hardness, nickel, copper, fluoride and other halides, sulfate, nitrate, and sulfide. Their major advantage for water analysis are their speed and ability to be used for in situ monitoring. However, as with glass pH electrodes, there are potential interferences which must be recognized and adjustments made when necessary. Similarly, since they are electrochemical sensors, they measure activity, rather than concentration.

The experimental procedure in their use is also quite similar to that of the glass pH electrode. They are used with a reference electrode, such as saturated calomel or silver-silver chloride, and a high impedance potential measuring device, such as a pH meter with a millivolt scale. A calibration plot of voltage versus the logarithm of concentration of the test ion is made, generally for at least a 10 fold range of concentration, and the measured voltage for the test solution measured, the test ion concentration then being calculated from the calibration plot.

Using the calcium electrode, for example, the calibration curve in the absence of interfering ions should follow the equation

$$E = \text{const.} + RT/2F \ln (Ca^{++}) \qquad \text{(X-6)}$$

with E as the measured cell voltage, R the gas constant, T the absolute temperature, F the Faraday, and (i) the activity of an i species. For dilute solutions, or those in which the ionic strength is constant, concentration, represented by [i], may be substituted for activity and Equation (X-6) at 25°C becomes

$$E_{CELL}\ (mv) = \text{const.} + 30 \log [Ca^{++}] \qquad (X\text{-}7)$$

However, it should be noted that the theoretical value of 30 mv for the slope of dE/d log $[Ca^{++}]$ is usually not obtained, and it is necessary to calibrate to be certain of the value. Also the activity and concentration may not be equal, because the solution is not sufficiently dilute, or they may not be related in the same way in the test and calibrating solution. In this case, it is frequently convenient to add electrolyte to all solutions to fix them at the same ionic strength prior to calibration and measurement.

Although ideally Equation (X-6) describes the behavior of the calcium electrode, other cations may interfere with its use. For one commercially available calcium electrode (22) interferences from Mg^{++}, Ba^{++}, H^{+}, and Na^{+} affect the cell potential according to the equation

$$E_{CELL} = \text{const.} + 30 \log \{ (Ca^{++}) + 0.014(Ba^{++}) + 0.010(Mg^{++}) + 10^{5}(H^{+}) + 10^{-4}(Na^{+}) \} \qquad (X\text{-}8)$$

When a coefficient preceding a particular ion is larger than unity, the electrode is more sensitive to that ion than it is to calcium; the reverse also holds. Thus, the calcium electrode is very sensitive to H^{+} and cannot, therefore, be used at low values of pH. Similarly, Equation (X-8) indicates that, for example, a 0.2M solution of Mg^{++} will give the same reading as 0.002M solution of Ca^{++}. Thus, low levels of magnesium are readily tolerated and do not

interfere with intermediate levels of calcium being measured. No electrode should be used without considering such possible interferences.

In using these electrodes to determine the concentration of a test ion, the possibility exists that not all of the soluble species being measured is available as a free ion, unassociated with other solutes. Thus, in the use of the fluoride electrode at low pH, it should be noted that, due to the fact that HF is a weak acid with a pH of 3.14, some of the fluoride will be bound to hydrogen ions and not sensed by the electrode; raising the pH will obviate this problem. Complexation of fluoride by aluminum poses a similar difficulty. Calcium and magnesium ions may also be complexed or otherwise bound to ions in natural waters.

All ion selective electrodes have limited sensitivity, usually dependent upon the finite solubility of its sensitive membrane. Thus, this material dissolves at the electrode surface and is sensed by the electrode itself. Although they may require somewhat more care and sophistication in use and interpretation than do pH electrodes, ion selective electrodes are, nevertheless, a powerful tool in water analysis.

E. Polarography

Polarography is a useful tool in the analysis of metal ions in water because of its high sensitivity, and its ability to analyze mixtures, reducing the need for prior separations, and to tolerate large quantities of dissolved solids, such as in brines and sea water. A variety of polarographic techniques have been utilized in water analysis and their ranges and advantages reviewed (18). One study of conventional polarography for the analysis of copper, cadmium, zinc, chromium, and lead in river water, sewage and sewage effluents concluded that in general, it was as sensitive as many good colorimetric analyses, yet was advantageous because it was simpler and separation techniques were not required (3).

A comparison of the various polarographic techniques indicates that conventional polarography with the dropping mercury electrode is sensitive in the range of 10^{-5}M; pulse polarography around 10^{-7}

to 10^{-8}M; cathode-ray polarography better than 10^{-7}M and is widely used in water analysis; and anodic stripping polarography sometimes better than 10^{-9}M because of its pre-concentration feature (18). It was also indicated that a combination of cathode-ray and anodic stripping voltammetry appeared to offer excellent sensitivity, one such reported application for zinc analysis in sea water having a sensitivity of 1 µg/l.

An example of the analysis of copper and zinc in river water was given using cathode-ray polarography (18). Samples of 100 to 500 ml were filtered and evaporated with perchloric acid to destroy organic matter, diluted with buffer and supporting electrolyte to 5 or 10 ml, and the analysis performed without further separation, copper at -0.4 volts and zinc at -1.2 volts vs. a mercury pool anode, respectively. In another example, cathode-ray polarography was used to analyze the quality of a central supply of distilled water for a laboratory. After concentrating by factors of 10 to 100, copper in the range of 0.5 to 4.0 µg/l, lead from 0.6 to 8.0 µg/l, and zinc at 5.0 µg/l were determined simultaneously.

In the analysis of river water and brine, samples were evaporated to dryness, while sewage in addition, was ashed to destroy organics (3). The residues were then redissolved and the additions made of the appropriate electrolyte, buffer, and, where necessary, maxima suppressor, such as polyelectrolyte, and sulfite to reduce oxygen. Using this procedure and conventional polarography for river water samples to which was added 0.10 mg/l each of copper, cadmium, zinc, chromium, and lead, the recovery was generally complete within 10% and the standard deviation was 4-5%, except for cadmium which was 9%. Similar results were obtained for brine. The authors noted that the polarograph wave height for a well formed wave could be measured with a precision of 0.005 mg/l, but not for small metal concentrations of the order of 0.01 mg/l. They suggested improvement of sensitivity by extraction with dithizone, followed by its destruction before polarographic analysis.

Because of their applicability to a large number of metals and their advantages cited above, the various polarographic methods present another series of important analytical tools for determining both trace and macro quantities of elements in a wide range of waters.

F. Other Flame Techniques

Although atomic absorption spectrophotometry is now widely used for a multitude of metals in water analysis, flame photometry is nevertheless a useful technique for the alkali and alkaline earth metals, although more sensitivity can be obtained for the former. For other metals, flame photometry can be used, but the sensitivities are much poorer than for colorimetric and other instrumental techniques.

For the determination of many alkali and alkaline earth elements by flame photometry in such a multicomponent system as sea water, it is generally necessary to separate the test ion prior to analysis, due to interferences both from major elements like sodium, as well as minor elements where emission spectra overlap with that of the test ion. Also for most accurate analysis, it is often necessary to add a known amount of an internal standard to the test ion colution to eliminate variability in the flame characteristics.

In one scheme of analysis for the major cations in sea water, the test solution was adsorbed onto a cation exchange resin which was eluted by a successive displacement technique, the strontium then being analyzed by flame photometry after being separated from the potassium, sodium, magnesium, and calcium (11). Lithium has been similarly analyzed in sea water after being separated from other alkali metals and alkaline earths (24), as have such ions as potassium (21), strontium and barium (2).

In addition to interferences due to emission from other elements, there are also interferences as a result of suppression of emission and the effects of foreign constituents on solution viscosity, surfacetension and volatility. Nevertheless, with care and the use of separation techniques when necessary, flame photometry can be a useful analytical tool, especially for the alkali metals.

Another potentially useful flame technique which has been developing in recent years is atomic fluorescence flame spectrometry (7). This method depends on the excitation of neutral atoms in a flame by an outside source of light, such as a zenon arc lamp, and the subsequent measurement of the emission intensity. There is evidence that in some cases the sensitivities obtained by this

technique are much greater than for other flame methods. For example, the limits of detection for analysis by this fluorescence technique as compared to AAS were for cadmium 0.2 versus 10 µg/l; mercury, 100 versus 500; thallium, 40 versus 200; and zinc, 0.1 versus 5 (7). Nevertheless, atomic fluorescence flame photometry is a relatively new technique and has not been widely used in water analysis.

G. Emission Spectroscopy

Direct current arc emission spectroscopy has been used for the analysis of many metals in a variety of natural and treated waters, particularly the trace elements. This technique is not sufficiently sensitive for most trace metals and, therefore, there must be preconcentration prior to analysis, such as by evaporation, precipitation and ion exchange (14,13). The method can tolerate large quantities of dissolved solids, although such macro elements as sodium, potassium, calcium and magnesium do interfere with the trace elements. However, this can be compensated by adding these elements to the standards.

In one routine use of this spectroscopic technique in analyzing a large number of samples from surface waters in the United States, all samples are reduced so as to provide the same total quantity of solid material in the dried residue arced in the spectrograph, giving a constant matrix (14). Thus, since the untreated samples contain variable amounts of dissolved solids, the concentration factor and, hence, the sensitivity of the method vary accordingly. However, in using a chelation-precipitation technique to separate the trace metals from the macro elements, the sensitivity was said to be adjustable at will, since a wide choice of preconcentration factors was available (23). However, in this case, the precipitation-separation operation was time consuming.

In many cases, the sensitivity of arc emission spectroscopy without preconcentration is not as good as with other techniques. However, the method is suitable for analyzing a large number of samples. For a variety of surface water systems in the United States, the method of preconcentration by evaporation resulted in

the following detection limits in µg/l: Ag and Be, 0.03 to 0.2; Ba, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Cd, Co, Sn, 1 to 20; Bi and Sb, 5 to 60; and Zn, 300 to 3500 (14).

H. Neutron Activation Analysis

Neutron activation analysis is a very sensitive technique for metal analysis, but requires the use of elaborate and expensive equipment which is not generally available to most laboratories (14). Examples of sensitivities are gold, 0.0004 µg/l; platinum, 0.1; zinc, .006; cobalt 0.0006; and copper 0.003. In addition to the disadvantage of requiring specialized equipment, neutron activation analysis also frequently requires elaborate separation processes, both for the purpose of eliminating interferences prior to irradiation, but also subsequently in order to measure separately the radioactivity of each of several elements in a complex mixture.

An example of the application of this technique is the analysis of fifteen lanthanide elements in sea water, the range of concentrations being 0.00013 to 0.0133 µg/l (13). In this method, iron and uranium were separated from the lanthanides by ion exchange and precipitation was used for preconcentration. After irradiation with neutrons, gradient elution by ion exchange was used to separate the activated products and beta counting performed on the separate fractions. It was found that the variation in lanthanide concentration among the oceans was great. For example, the Indian Ocean had total lanthanide concentrations about 100 times that of the deep Central Atlantic Ocean.

REFERENCES

1) J. B. Andelman, J. Water Poll. Control Fed., 40, 1844 (1968).

2) N. R. Anderson and D. N. Hume, "Trace Inorganics in Water," R. F. Gould, ed., Chapt. 18, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

3) D. G. Ballinger and T. A. Hartlage, Water Sewage Works, 110, 31 (1962).

4) D. G. Biechler, Anal. Chem., 37, 1054 (1965)

5) Y. Chau, S. Sim, and Y. Wong, Anal. Chim. Acta, 43, 13 (1968).

6) J. M. Chilton, Anal. Chem., 25, 1274 (1953).

7) D. W. Ellis and D. R. Demers, "Trace Inorganics in Water," R. F. Gould, ed., Chapt. 20, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

8) G. M. Fair, J. C. Geyer, and D. A. Okun, "Water and Waste Engineering," vol. 2, John Wiley and Sons, Inc., New York, 1968.

9) M. J. Fishman and M. R. Midgett, "Trace Inorganics in Water," R. F. Gould, ed., Chapt. 12, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

10) R. M. Garrels and M. E. Thompson, Am. J. Sci., 260, 57 (1962).

11) R. Greenhalgh, J. P. Riley, and M. Tongudai, Anal. Chim. Acta, 36, 439 (1966).

12) J. D. Hem, U. S. Geological Survey Water-Supply Paper 1459-B, Washington, D.C., 1960.

13) O. T. Hogdahl and S. Melsom, "Trace Inorganics in Water," R. F. Gould, ed., Chapt. 19, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

14) D. N. Hume, "Equilibrium Concepts in Natural Water Systems," R. F. Gould, ed., Chapt. 2, Advances in Chem. Series No. 67, American Chemical Society, Washington, D.C., 1967.

15) J. L. Jones and R. D. Eddy, Anal. Chim. Acta, 43, 165 (1968).

16) H. L. Kahn, "Trace Inorganics in Water," R. F. Gould, ed., Chapt. 11, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

17) R. C. Kroner and J. F. Kopp, J. Am. Water Works Assoc., 57, 150 (1965).

18) E. J. Maienthal and J. K. Taylor, "Trace Inorganics in Water," R. F. Gould, ed., Chapt. 10, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

19) J. C. Morris and W. Stumm, "Equilibrium Concepts in Natural Water Systems," R. F. Gould, ed., Chapt. 13, Advances in Chem. Series No. 67, American Chemical Society, Washington, D.C. 1967.

20) J. A. Platte, "Trace Inorganics in Water," R. F. Gould, ed., Chapt. 14, Advances in Chem. Series No. 73, American Chemical Society, Washington, D.C., 1968.

21) J. P. Riley and M. Tongudai, Chem. Geol., 1, 291 (1966).

22) J. W. Ross, Science, 156, 1378 (1967).

23) W. D. Silvey and R. Brennan, Anal. Chem., 34, 784 (1962).

24) Z. Sulcek, P. Povondra, and R. Stangl, Chemist-Analyst, 55, 36 (1966).

25) A. M. Tenny, Perkin-Elmer Instr. News, 18, 1 (1967).

26) M. E. Thompson, Science, 153, 866 (1966).

27) M. E. Thompson and J. W. Ross, Science, 154, 1643 (1966).

XI. ANALYSIS FOR INORGANIC ANIONS

Discussion in this section is directed to the analysis of non-metal inorganic species including nitrogenous compounds and phosphates, which are frequently classified as biochemical nutrients.

A. Separation and Concentration Techniques

The techniques discussed for separation and concentration of metal ions are generally applicable also for non-metal inorganic species. Evaporation, precipitation, ion exchange, solvent extraction, and partial freezing are frequently used ion exchange being particularly well suited for anion separations. Anion exchange chromatography has been used rather extensively for separations of species found in waters and wastewaters ([1]). Silicates, for example, can be effectively separated from natural waters by treating with hydrogen fluoride to form fluorosilicates, which are then removed by exchange ([2]).

Techniques for the chromatographic separation of ortho-, pyro-, tri-, trimeta-, tetrameta-, and polyphosphates have been developed ([3] , [4]) with strongly basic anion exchange resins. Potassium chloride, in continuously increasing concentration (gradient elution technique) is used for elution. Sulfate, sulfite, thiosulfate and sulfide ions can be separated by anion exchange chromatography using the gradient elution technique with an elution solution of nitrates ([5]). A more detailed discussion of the possible applications of anion exchange for such analytical separations has been given by Inczedy ([6]).

B. Instrumental Methods

A number of instrumental methods are applicable to the analysis of non-metallic inorganic species in natural waters and wastewaters. Many such analytical methods involve either the use of potentiometric membrane electrodes or the application of spectrophotometric techniques. New methods of absorption spectro-

photometry using solid-phase ion (or ligand) exchange reagents have been devised for analyses for chloride, sulfates, phosphates and other anions (7 , 8 , 9). These tests are based on using various salts of chloranilic acid as selective ion exchange reagents. Typical examples include the analysis for sulfates with barium chloranilate (7), for chlorides with mercuric chloranilate (8) and for phosphates with lanthanum chloranilate, i.e.,

$$BaCh + SO_4^{2-} \longrightarrow BaSO_4 + Ch^{2-} \qquad (XI\text{-}1)$$

$$HgCh + 2Cl^- \longrightarrow HgCl_2 + Ch^{2-} \qquad (XI\text{-}2)$$

$$La_2Ch_3 + 2PO_4^{3-} \longrightarrow 2LaPO_4 + 3Ch^{2-} \qquad (XI\text{-}3)$$

This technique is subject to interferences which may be reduced by solvent extraction.

Many highly sensitive methods for non-metallic inorganic species are based on the displacement of a ligand (usually colored) in a metal complex or chelate. The analysis for fluoride ions by displacement of a chelating dye anion from a zirconium complex is a typical example of this technique. The displaced dye differs sufficiently in color from its zirconium chelate to permit determination of the fluoride ion concentration as a function of the change in color of the solution (10).

Numerous indirect spectrophotometric methods have been developed (11). Heteropoly chemistry appears to offer important advances in analyses for phosphates, silicates and arsenates (12). The reader is referred to recent reviews in Anal. Chem. for exhaustive survey on the subject matter (11).

Indirect UV spectrophotometry and atomic absorption methods have been developed for phosphates and silicates (13). These techniques are based on the selective extraction of molybdophosphoric acid and molibdosilicic acid, followed by ultraviolet molecular absorption spectrophotometry and/or atomic absorption spectrophotometry. The molybdophosphoric and molybdosilicic acids

are formed in acidic solution by addition of excess molybdate reagent. Molybdophosphoric acid is extracted with diethyl ether from an aqueous solution which is approximately 1M in hydrochloric acid. After adjusting the hydrochloric acid concentration of the aqueous phase to approximately 2M, the molybdosilicic acid is extracted with 5:1 diethyl ether-pentanol solution. The extracts of molybdophosphoric and molybdosilicic acids are subjected to acidic washings to remove excess molybdate. Each extract is then contacted with a basic buffer solution to strip the heteropoly acid from the organic phase. The molybdate resulting from the decomposition of the heteropoly acid in the basic solution is then determined either by measurement of the absorbance at 230 mμ using ultraviolet spectrophotometry or by measurement of absorbance at the 313.3 mμ resonance line of molybdenum by atomic absorption spectrophotometry. The optimum concentration ranges are approximately 0.1-0.4 mg/l of phosphorus or silicon for indirect ultraviolet spectrophotometry and 0.4-1.2 mg/l for indirect atomic absorption spectrophotometry.

Electrochemical methods of analysis offer considerable promise for selective and specific measurements in wastewaters. Direct potentiometric techniques using electrode of the second kind may be used for the analysis of chlorides or sulfides. Silver electrodes, coated with a layer of halides or sulfides, are available commercially for determination of chlorides, bromides, iodides, and sulfides at concentrations corresponding to the solubilities of the respective silver salts, as given by the following expressions:

$$E_{cell} = E^{\circ}_{Ag^+,Ag} - E_{ref} + \frac{RT}{ZF} \ln K_{sp} - \frac{RT}{ZF} \ln Cl^- \qquad \text{(XI-4)}$$

and

$$E_{cell} = E^{\circ}_{Ag^+,Ag} - E_{ref} + \frac{RT}{ZF} \ln K_{sp} - \frac{RT}{ZF} \ln S^{2-} \qquad \text{(XI-5)}$$

where K_{sp} refers to the solubility products of AgCl and Ag_2S,

respectively in Equations (XI-4) and (XI-5). Limitations on the use of such electrode systems are imposed by interferences from other potential-determining ions, by the problem of elimination of liquid junction potentials, and by the difficulty of satisfactorily resolving single ion activity coefficients.

Major developments in electrochemical analysis for anions have occurred in the area of ion-selective electrodes. Such electrode systems are primarily solid state or precipitate, ion exchange membrane electrodes. Pungor and co-workers (14) have developed anion selective membrane electrodes by impregnating silicone gum rubber membranes with specific insoluble salts. Electrodes which are selective for Cl^-, Br^-, I^-, S^{2-}, SO_4^{-2} and F^- have been reported (15 , 16). Pungor (15) has reviewed the literature of ion selective membrane electrodes and discussed the preparation and characterization of the membrane. Response time, memory effects, and detection limits up to 10^{-4} M have been discussed. Detailed studies on the sensitivity and selectivity of iodide, bromide and chloride electrodes has been reported by Rechnitz, et al (17 ,18). The electrodes were prepared by incorporating AgI, AgBr, and AgCl, into silicone rubber matrices. Selectivity ratios for the various electrodes were reported with response times ($t_{1/2}$) of 8, 14, and 20 seconds, respectively. The lower limits of response (Equation XI-6) were 10^{-7}M I^-, 5×10^{-4}M Cl^-, and 7×10^{-5}M Br^-.

$$E = \text{const.} + RT/F \ln \{ {}^{\alpha}A^+ + K{}^{\alpha}B^+ \} \qquad \text{(XI-6)}$$

where ${}^{\alpha}A^+$ and ${}^{\alpha}B^+$ are the activities of A^+ and B^+ ions, respectively, and K is a selectively constant which expresses the realtive sensitivities of the glass electrode for ions B^+ and A^+.

Electrode systems prepared by incorporating metal oxides and hydroxides (19) or ion exchange resins (14) in polymeric membranes also have been reported. Solid state ion exchange membrane electrodes for fluoride ion determinations have been reported (20). This type of membrane electrode is made of single crystals of

LaF_3, NdF_3, and PrF_3 and is reported to be sensitive to fluoride ion concentrations as low as 10^{-5}M.

Anion selective membrane electrodes can be used for direct potentiometry or for potentiometric titrations. For example, Lingane (21) used a commercially available fluoride electrode for the potentiometric titrations of Th^{4+}, La^{3+} and Ca^{2+} ions. Best results were obtained with $La(NO_3)_3$. The equivalence point potential was determined within ±2mV and an accuracy better than 0.1% was noted in neutral, unbuffered solutions.

Cathodic stripping voltammetry can be also used for trace analysis of halides (22). Brainina and co-workers (23) have compared the limits of sensitivities of various anions using mercury electrodes, and have given concentration limits of 5×10^{-6}M for Cl^-, 1×10^{-6}M for Br^-, and 5×10^{-6}M for I^-.

C. Sulfur Compounds

Sulfides commonly occur in a variety of waste effluents (e.g., septic sewage, oil refinery wastes, tannery wastes, viscose rayon wastes, etc.). The presence of sulfides in wastewaters is usually indicated by the characteristic odor of hydrogen sulfide. The acidity constants for the diprotic acid, H_2S, are $K_1 = 1.0 \times 10^{-7}$ and $K_2 = 1.2 \times 10^{-13}$.

Detection of free sulfides in wastewaters is relatively straightforward; a small sample volume is placed in 150 ml glass-stoppered conical flask and slightly moistened lead acetate paper is suspended between the stopper and the neck. On acidification of the sample, a brown stain on the paper indicates the presence of sulfides. As low as 0.01 mg/l H_2S in a 50 ml sample can be detected in this manner.

Total sulfides may be accurately determined in the range from 0.1 to 20 mg/l H_2S, by standard molecular absorption spectrophotometry (24). The test is based on the fact that hydrogen sulfide and sulfides react with p-aminodimethylaniline hydrochloride in the presence of sufficient hydrochloric acid and an oxidizing agent (ferric chloride) to produce methylene blue dye. The test is sensitive to free sulfides as well as sulfides bound by iron,

manganese and lead. Sulfides of copper and mercury are too insoluble to react. Sulfites and thiosulfates interfere, but by increasing the amount of ferric chloride and lengthening the time of reaction, up to 50 mg/l of these compounds may be tolerated.

Sulfides in industrial waste effluents may be precipitated by adding zinc or cadmium acetate or ammoniacal zinc chloride. The precipitated sulfide is then added to excess acidified standard iodine solution which is back-titrated with standard thiosulfate (25). Several modifications of iodometric determinations of sulfides in wastewaters have been reported (26 , 27).

The methods of analysis for sulfides described above give total sulfides; i.e., free and bound sulfides, polysulfides, and sulfanes. A specific test for only free sulfides can be accomplished using specific ion exchange membrane electrodes (28).

Specific ion electrode potential measurements of S^{2-} can be related to the concentrations of H_2S, HS^-, and S_T (analytical concentration of free sulfides) by the following equilibrium relationship

$$\log [S_T] = \log [S^{2-}] + \log \left[\frac{[H^+]^2}{K_1 K_2} + \frac{H^+}{K_1} + 1\right] \qquad \text{(XI-7)}$$

$$\log [H_2S] = \log [S^{2-}] + \log \frac{[H^+]^2}{K_1 K_2} \qquad \text{(XI-8)}$$

$$\log [HS^-] = \log [S^{2-}] + \log \frac{[H^+]}{K_1} \qquad \text{(XI-9)}$$

where K_1 and K_2 are the acidity constants for the weak acid H_2S.

Sulfites are commonly found in the wastewaters from pulp and paper mills, in which sulfites are used for the preparation of cellulose from wood. In the absence of thiosulfates, sulfites can be detected by heating an acidified water sample and identifying the evolved sulfur dioxide by the blue coloration produced when subjected to a piece of filter paper moistened with a mixture of potassium iodate solution and starch solution. Sulfites also

may be detected in waste effluents by decolorization of triphenylmethane dyes by neutral sulfite solutions.

The iodometric titration of sulfites is done after sulfides are precipitated and filtered as zinc sulfides. This test is subject to interferences from organic matter and other reduced compounds, such as ferrous iron, in the test solution.

Sulfate determination in wastewaters is not called for except in connection with problems associated with corrosion of concrete pipes. Sulfates may be determined gravimetrically or turbidimetrically when precipitated as barium sulfate (29). Sulfites, sulfides, silica and other insoluble solids may interfere with the gravimetric procedure. Turbidimetric measurements of $BaSO_4$ may be improved by using glycerin and sodium chloride to stabilize the suspension.

Titrimetric analysis of sulfates may be done by first precipitating the sparingly soluble benzidine sulfate, followed by titration of the washed precipitate with standard sodium hydroxide using phenolphtholein as an indicator (30). Interferences by phosphates can be minimized by using a colorimetric technique. The precipitated benzidine sulfate is washed with an alcohol-ether mixture to remove excess benzidine, dissolved in 1% sodium borate and the liberated benzidine is allowed to react with 1:2 naphthoquinone-4 sulfonate to give a red color which is determined photometrically at 290 m (31).

Sulfate ions can also titrated in an alcoholic solution under controlled acid conditions with a standard barium chloride solution using thorin as an indicator. This test can be extended by use of ion exchange separation and concentration techniques. A number of anions and cations may cause interferences (e.g., potassium, iron, aluminum, phosphates, fluorides, and nitrates). Most metallic ions also interfere by forming colored complexes with the thorin indicator, especially in the alcohol-water solution. It is sometimes necessary to use ion exchange separation to remove interferences prior to sulfate titration (32).

D. Cyanides, Thiocyanates and Cyanates

Cyanides may be found in significant quantities in industrial wastewaters from electroplating, steel, coke ovens, gold mining, and metal finishing industries. Cyanides are extremely toxic, even in low concentrations. In view of their toxicity, they can be detected easily by fish-kill incidence in concentrations as low as 0.03 mg/l HCN.

Hydrogen cyanide is a volatile weak acid ($K_a = 4.8 \times 10^{-10}$). Both HCN and the conjugate base, CN^-, are called "free cyanides." Stable cyanide salts and metal cyanide complexes, such as $K_4Fe(CN)_6$ and $K_3Co(CN)_6$, also may be found in waste effluents. Total cyanide determinations include both free cyanides and complexed cyanides. The test for total cyanides ([29]) is usually done by breaking down complex metal cyanides by distillation with (a) hydrochloric acid solution of cuprous chloride; (b) tartaric acid, (c) mercuric chloride, magnesium chloride and sulfuric acid ([33])(serfass method), and (d) phosphoric acid in the presence of citric acid and ethylene diamine tetra acetic acid ([34]).

A simple procedure for detecting cyanides in a wastewater is based on treating a strip of filter paper with a drop of 10% ferrous sulfate and a drop of 10% caustic soda, and suspending the paper strip over the acidified sample solution in a glass stoppered flask for about 10 minutes. The liberated HCN reacts to form ferrocyanide on the paper which, when the paper is immersed in hot dilute hydrochloric acid, yields the blue to blue-green stain of prussian blue dye. This test is sensitive to about 0.4 mg/l of HCN.

Traces of cyanides can be determined by the Aldridge Test, frequently known as the bromin-pyridine-benzidine method ([35]). The procedure utilizes the Konig synthesis, which is based on converting cyanide to cyanogen bromide (or chloride) and the reaction with pyridine and on aromatic amine (benzidine) to give an intense characteristic color. The di-anil derivative formed (orange to red) may be determined spectrophotometrically. Thiocyante will give the same reaction as cyanides with this test. Interference due to thiocyanide may be minimized by extracting cyanides from acid solution with isopropyl ether, which can be

recovered by extraction in an aqueous sodium hydroxide solution (34). An alternate procedure (31) is based on cyanide conversion to cyanogen chloride by chloramine-T, which is allowed to react with pyridine containing 1-phenyl-3-methyl-5-pyrozolone to give a blue color which is determined spectrophotometrically (29).

A very sensitive and accurate method for the analysis of cyanides is based on the interaction of "ferroin" with cyanides at pH 9.2-9.7 (36). The violet complex [dicyano-bis-(1:10-phenanthroline)-iron] formed is extracted with chloroform and determined spectrophotometrically. This procedure is claimed to be subject to fewer interferences than any of the other methods discussed previously.

One of the oldest procedures for the analysis of cyanides in waste effluents is the Liebig test (29). This is based on the titration of cyanides with silver nitrate to form a soluble argentocyanide complex, $[Ag(CN)_2]^-$. After all cyanides have reacted, excess silver nitrate will cause turbidity due to precipitation of silver cyanide. The end point is characterized by the first appearance of turbidity, which in most cases is difficult to detect by eye. A colorimetric indicator, p-dimethylaminobenzylidine-rhodanine in acetone, can be used to aid in detection of the titration end point. In alkaline solution (pH 10-11) the end point will be characterized by a change of color from yellow to salmon-pink. Dithizone may be also used for this titration (36).

Thiocyanates and cyanates are frequently present in plating and gas-works waste effluents. The cyanates may be easily detected by their interaction with ferric chloride in hydrochloric acid solution to give a characteristic wine-red color. This test is very approximate in nature and is subject to various interferences, such as those caused by mercury salts, fluorides, organic hydroxy acids, etc. (37).

Thiocyanates, if present in relatively large quantities, can be estimated by precipitation as cuprous thiocyanate, which is either titrated with standard potassium iodate in acidic solution in the presence of chloroform or is decomposed with caustic soda, acidified with nitric acid and titrated with silver nitrate using alum as indicator (25).

Thiocyanates may be determined colorimetrically in trace quantities by the formation of the copper pyridine thiocyanate complex, $[Cu(C_5H_5N)_2\ (CNS)_2]$, which can be extracted in chloroform to yield a yellow solution (38). The test is sensitive to 0.5 mg/l CNS^- and is subject to interferences from cyanides. Cyanides may be removed by acidifying the solution with acetic acid and stripping HCN by aeration.

Cyanates may be determined by hydrolyzing the cyanates to ammonia by boiling with acid, and estimation of ammonia so formed by means of Nessler's reagent (39). Any ammonia originally present in the sample should be removed.

E. Chlorides

Chlorides are present in large quantities in certain pickle liquors, in spent regenerant solutions from softening plants, oil well waters, drainage from irrigation waters, and other waste effluents.

The terms "salinity" and "chlorinity" are frequently used to express chloride content in marine and estuarine waters. "Salinity" is defined as the weight in grams of dissolved solids (dried to constant weight at 480°C to remove organic matter and to convert carbonates to oxides) in 1000 grams of sea water. "Chlorinity," on the other hand, is defined as the weight of halides, as measured by reaction with silver nitrate and computed on the basis of all halides being represented as chlorides. Both salinity and chlorinity are commonly expressed in parts per mille and are related in sea water as follows:

$$S°/_{oo} = 0.03 + 1.805\ Cl°/_{oo} \qquad \text{(XI-10)}$$

where $S°/_{oo}$ and $Cl°/_{oo}$ refer to parts per mille salinity and chlorinity, respectively.

One procedure for chlorides in wastewaters is by titration with silver nitrate. In this method, which is commonly referred

to as the Mohr method, the end point is detected by the formation of reddish silver chromate by the slightest excess of silver. The test is subject to interferences from substances such as sulfides, thiocyanides, phosphates, cyanides, sulfites, acids, alkalies and any anion which may form a sparingly soluble silver salt. Some of these interferences can be eliminated by adjustment of pH or by potentiometric titration with a silver wire indicator electrode and a glass electrode as a reference (40). Volatile sulfur compounds which may be present in wastewaters from oil refineries and synthetic rubber manufacturing may be removed by evaporation. Sulfides and thiocyanates may be destroyed by addition of hydrogen peroxide and heating.

If the test solution contains large quantities of phosphates, the Volhard procedure is recommended (29). This involves addition of an excess of silver nitrate to a sample which has been acidified with dilute nitric acid, followed by coagulation of the silver chloride by shaking with nitrobenzene, and, finally, back titration with standard thiocyanate using gerric alum as indicator.

Titration of chloride with mercuric nitrate offers a more sensitive procedure (29). The test is based on titration with mercuric nitrate to form a slightly-dissociated mercuric chloride complex in an acid solution (pH $\approx$ 3.0). The end point is detected by the mixed indicator diphenylcarbazone and bromophenol blue, which turns blue-violet upon addition of a slight excess of mercuric ion.

F. Fluorides

Fluorides occur in the wastewaters of industries involved in the production of aluminum from bauxite, the production of phosphatic fertilizers, in oil field effluents, in nuclear power plant effluents, and in wastewaters from the scrubbing of blue gases and from the etching of glass.

Fluorides may be titrated with standard thorium nitrate in a solution buffered at pH $\approx$ 3.0 (41). Sodium alizarin sulfonate, solochrome brilliant blue and chrome azurol S have been used as end point indicators (41, 42). Interferences from sulfate phosphate and carbonate can be minimized by sample pretreatment

with barium chloride.

The most populat method of fluoride analysis is based on the bleaching action of fluorides on the reddish lake formed by zirconium oxychloride and sodium alizarine sulfonate ([43]). Visual color comparison is usually done with the zirconium alizarin test ([29]). Both color intensity and hue vary with fluoride concentration. A more stable color complex is formed with fluorides and zirconium-eriochrome cyanine R ([29]). The color intensity of the complex is diminished by addition of F^- and is measured spectrophotometrically at 540 mμ

The preceding colorimetric procedures are subject to numerous interferences commonly found in industrial wastewaters. It is therefore recommended that fluorides be separated by distillation or ion exchange ([29]) prior to analysis by the above procedures.

Probably the most simple as well as direct method for the analysis for fluoride ions is that based on the use of potentiometric membrane electrode systems. Lanthanum fluoride membrane electrodes have been used with considerable success for direct determination of fluorides in water supplies ([20]) and industrial wastewaters ([21]). It is also possible to use lanthanum fluoride membrane electrode systems for precise end point detection in the titration of fluoride ions with calcium or other fluoride complexing agents ([21]).

Hydroxide ions at high concentrations interfere with the lanthanum fluoride electrode sensitivity, which limits its application at high pH values. Similar to other potentiometric membrane electrode systems the sensitivity is in the range of 10^{-6} MF^- or 0.02 ppm.

G. Nitrogen Compounds

Analysis for Combined Nitrogen (Ammonia, Nitrites and Nitrates) NH_3, NO_2^- and NO_3^- in wastewaters may result from the degradation of organic nitrogenous compounds or may be entirely of inorganic origin.

The most widely used method for analysis for ammonia is the Nesslerization reaction. The test is based on the development of a

yellow-brown (colloidal) color on addition of Nessler's reagent to an ammonia solution. The standard method (48) and the ASTM reference test (47) recommend the separation of the ammonia from the sample by distillation prior to the Nesslerization reaction. Direct Nesslerization is most often preferred, however, for rapid routine determinations.

For certain industrial wastewaters, it is often desirable to distinguish between "free" ammonia and "fixed" ammonia. The former is estimated by a straightforward distillation; the residual liquor is then treated with an alkali (e.g., sodium carbonate, magnesium oxide or caustic soda) and distilled to determine fixed ammonia. Certain substances interfere with both the direct Nesslerization and distillation methods, e.g., glycine, urea, glutamic acid, acetamides and hydrazines.

The standard method (47 ,48) for nitrites in water is based on forming a diazonium compound by the dizaotization of sulfonilic acid by nitrite under strongly acidic conditions and coupling with alpha-naphthylamine hydrochloride to produce a reddish-purple color. Spectrometric measurement of the color of the azo dye is performed at 520 mμ, or visual comparison with standards may be used. This method is sometimes known as the Griess-Ilosvay method (49). A frequently used alternative procedure for nitrite is based on formation of a yellowish-brown dye by the reaction of nitrite in acid solution with meta-phenylene diamine (50).

The Griess-Ilosvay method is most suitable for low nitrite concentrations, e.g., below 2.0 mg/l. Another colorimetric procedure which is more suitable at high concentration involves reaction of the nitrites with meta-phenylene diamine in an acid solution to form a yellowish-brown dye. Chlorides in concentration below 500 mg/l have no effect on either of the two procedures. High chloride concentrations (10,000 mg/l) interfere more with the Greiss-Ilosvay test. More distinct, pH-independent, color development is achieved (51) by replacing the sulfanilic acid with fulfanilamide and alpha-naphthylamine with 1-naphthyl-ethylene diamine dihydrochloride within the Griess-Ilosvay test. The sulfanilamide undergoes diazotization in hydrochloric acid and the

diazonium salt is then coupled with the diamine to give a stable red azo-dye.

An excellent review of approximately 52 spectrophotometric methods for nitrite has been reported by Sawicki et al. (52). The authors critically evaluate the sensitivity, color stability, conformity to Beer's law, simplicity and precision of a variety of methods. methods.

Colorimetry, UV spectrometry and polarography have frequently been used for nitrate determinations in natural waters and waste effluents. The phenoldisulfonic acid method and the brucine method are two colorimetric procedures more frequently used. In the former test, color development is based on the reaction between phenol disulfonic acid and nitrates in sulfuric acid solution to give a nitro-derivative which causes a yellow coloration when the solution is made alkaline; the intensity of the color is measures at 470 mμ. Nitrite ion interferes with the test in proportion to its concentration in the sample. Various inorganic ions have certain concentrations cause interference (47). Small amounts of chlorides do not interfere but nitrites should be removed with sodium azide (47).

An alternate test for nitrates involves reaction of a brucine solution in glacial acetic acid with nitrates and acidification with dilute H_2SO_4. The color intensity changes with time and it is necessary to develop the color of standards and samples simultaneously and compare maximum color intensity. Chlorides above 1,000 mg/l interfere with color development. Nitrites, if present, should be separately estimated and an appropriate correction applied. A salt-masking technique which renders the test applicable to sea water and brackish water has been proposed by Jenkins (53).

Nitrate analysis by reduction to ammonia, which is then detected by Nesslerization, has been reported by several authors. The procedure is based on expelling all ammonia from the water sample, followed by reduction of nitrogen (NO_2^- abd BI_3^-) by means of (a) aluminum foil in alkaline NaOH solution, (b) zinc-copper couple in acetic acid solution, (c) Dervado's alloy hydrazine (54), and (d) alkaline ferrous sulfates. The ammonia produced may be separated

by steam distillation and estimated in the distillate by Nesslerization. Various procedures have been proposed to minimize interferences due to nitrites and chlorides.

Nitrate analysis by reduction to nitrites which are then detected by the Griess-Ilsovay method has been applied to both natural waters and wastewaters (55). Controlled reduction of nitrates to nitrites is accomplished with zinc powder in acid solution.

Ultraviolet analysis for nitrates offers the advantage of freedom from chloride interferences and a variety of other inorganic ions. However, dissolved organic compounds, nitrites, hexavalent chromium, and surfactants interfere with this procedure. The test is based on measuring UV adsorption spectra of the filtered, acidified sample at 220 mμ. Measurements follow Beer's Law up to 11 Mg N/l. Interference of dissolved organics is estimated by doing a second measurement at 275 mμ, a wavelength at which nitrates do not absorb.

Simultaneous determination of nitrates, nitrites and sulfates in water samples by infrared techniques has been reported (53). The test is based on concentrating the sample by ion exchange and removal of phosphates, carbonates and organic matter. This is followed by separation by freeze drying the aqueous solution in the presence of KBr; the infrared spectrum is determined in the resulting KBr disk.

The polarographic analysis of nitrate is based on diffusion current measurements in an acid solution at -1.2 volts vs. the S.C.E. Nitrites, phosphates, ferric iron and fluorides interfere with the test. Procedures to minimize interferences have been prescribed. The polarographic test offers the advantage of being adaptable to continuous monitoring (47 ,48 ,56).

H. Analysis for Combined Phosphorus

Phosphorus may be present in industrial waste effluents either as inorganic phosphates (ortho-, meta-, or poly-phosphates) or in organic combination. The most common analytical method for inorganic

phosphorus is based on the colorimetric determination of the phosphomolybdenum blue complex (47 , 48). The test is specific for orthophosphates. Polyphosphates and metaphosphates are then estimated as the difference between total phosphates (hydrolyzed samples) and orthophosphates (non-hydrolyzed samples).

Orthophosphates react with ammonia molybdate in acid medium to form the phosphomolybdic acid complex, which when reduced yields the molybdenum blue color which may be determined colorimetrically. The sensitivity of the test is largely dependent on the method of extractions and reduction of the phosphomolybdic acid, aminonaphtholsulfonic acid (48), stannous chloride (Deniges Method) (37), metal sulfites (Tschopp reagent) (57), and ascorbic acid (58) have been used in the reduction step. The stannous chloride method is considered most sensitive and best suited for lower ranges of phosphate concentration.

A number of substances have been reported to interfere with the phosphate determination (48). Arsenic, germanium, sulfides, and soluble iron above 0.1 mg cause direct interferences. Tannins, lignins and hexavalent chromium will cause errors only for analysis of phosphate concentrations below mg/l.

REFERENCES

1. Westland, A.D., and R.R. Langford, Anal. Chem., 33, 1306 (1961).
2. Wickbold, R., Z. Analyt. Chem., 171, 81 (1959).
3. Weiker, W., Analyt. Chem., 185, 457 (1962).
4. Grande, J.A., and J. Beukenkamp, Analyt. Chem., 28, 1497 (1951).
5. Hurford, T.R., and D.F. Boltz, Abstracts of Papers, 154 American Chemical Soc. Meeting, Chicago (1967).
6. Inczedy, J., "Analytical Applications of Ion Exchangers," Pergamon Press, pp. 151 (1966).
7. Bertolacini, R.J., and J.E. Barney II, Anal. Chem., 29, 281 (1957).
8. Barney, J.E. II, and R.J. Bertolacini, Anal. Chem., 29, 1187 (1957).
9. Hayashi, K., T. Danzuka, and K. Ueno, Talanta, 4, 244 (1960).
10. Belcher, R., M.A. Leonard, and T.S. West, Talanta, 2, 92 (1954).
11. Boltz, D.F., and M.G. Mellon, Anal. Chem., 40, 255R (1968).
12. Crouch, S.R., and H.V. Malmstadt, Anal. Chem., 39, 1084 (1967).
13. Hurford, T.R., and D.F. Boltz, Abstracts of Papers, 154 American Chemical Soc. Meeting, Chicago (1967).
14. Pungor, E., K. Toth, and J. Havas, Acta Chim. Acad. Sci. Hung., 41, 239 (1964).
15. Punbor, E., and J. Havas, Acta Chim. Acad. Sci. Hung., 50. 77
16. Pungor, E., K. Toth, and J. Havas, Acta Chim. Acad. Sci. Hung., 48, 17 (1966).
17. Rechnitz, G.A., M.R. Kiesz, and S.B. Zamochnich, Anal. Chem., 38, 973 (1966).
18. Rechnitz, G.A., M.R. Kresz, Anal. Chem., 38, 1786 (1966).
19. Geyer, R., and W. Syring, Z. Chem., 6, 92 (1966).
20. Frant, M.S., and J.W. Ross, Science, 154, 1553 (1966).
21. Lingane, J.J., Anal. Chem., 39, 881 (1967).
22. Shain, I., and S.P. Perone, Anal. Chem., 33, 325 (1961).
23. Brainina, Kh.Z., J. Anal. Chem. (USSR), 19, 753 (1964).
24. Pomeroy, R., Sewage Works J., 8, 572 (1936).

25. Key, A., "Gas Works Effluents and Ammonia," Institute of Gas Engineers (London), 2nd ed. (1956).

26. Pomeroy, R., Petrolium Engr., 15, 156 (1944).

27, Houlihau, J.E., and P.E.L. Farina, Sewage Industr. Wastes, 24, 157 (1952).

28. Mancy, K.H., School of Public Health,The University of Michigan, Unpublished work (1968).

29. American Society of Testing Material, "Manual on Industrial Water and Industrial Waste Water," American Society for Testing Materials, 2nd ed. (1964).

30. Allen, L.A., J. Soc. Chem. Industr., 63, 89 (1944).

31. Kleeman, C.R., E. Taborsky, and F.H. Epstein, Proc. Soc. Exp. Biol., N.Y., 91, 480 (1956).

32, Fritz, J.S., and S.S. Yamamura, Anal. Chem., 27, 1461 (1955).

33, Serfass, E.J., R.B. Freeman, B.F. Dodge, and W. Zabban, Plating, 39, 267 (1952).

34. Kruse, J.M., and M.G. Mellon, Sewage Industrial Wastes, 23 1402 (1951).

35. Aldridge, W.N., Analyst, 69, 62 (1944).

36. Schilt, A.A., Analyt. Chem., 30, 1409 (1958).

37. Association of British Chemical Manufacturers and Society of Analytical Chemistry Joint Committee, Analyst, 83, 50 (1958).

38. Kruse, J.M., and M.G. Mellon, Sewage Industrial Wastes, 24, 1254 (1952).

39. Gardner, D.G., R.F. Muraca, and E.J. Serfass, Plating, 43 743 (1956).

40. Reilley, C.N., and D.T. Sawyer, Experiments for Instrumental Methods, McGraw-Hill Book Co., Inc. (1961).

41. Bond, A.M., and M.M. Murray, Biochem. J., 53, 642 (1953).

42. Milton, R.F., Analyst, 74, 54 (1949).

43. Lamer, W.L. and P.G. Drake, J. Am. Water Works Ass., 47, 563 (1955).

44. Front, M.S., and J.W. Ross, Anal. Chem., 40, 1169 (1968).

45. Front, M.S., Plating, 54, 702 (1967).

46. Lingane, J.J., Anal. Chem., 39, 881 (1967).

47. American Society of Testing Material, "Manual on Industrial Water and Industrial Waste Water," American Society for Testing Materials, 2nd ed. (1964).

48. APHA, AWWA, AND WPCF, "Standard Methods - Water and Waste-Water," American Public Health Ass., 12th ed. (1965).

49. Rider, B.F., and M.F. Mellon, Ind. Eng. Chem. (Anal.), 18, 96 (1946).

50. Klein, L.J., "Observations on the Determination of Nitrites in Sewage Effluents," J. Inst. Sewage Purif., 2, 153 (1950).

51. Shinn, M.B., Ind. Eng. Chem., 13, 33 (1941).

52. Sawicki, E., T.W. Stanley, J. Pfaff, and A.D. Amico, Talanta, 10, 641 (1963).

53. Jenkins, D., and L.L. Medsker, Anal. Chem., 36, 610 (1964).

54. Citron, I., H. Tsi, R.A. Day, and A.L. Underwood, Talanta, 8, 798 (1961).

55, Edwards, G.P., J.P. Pfafflin, L.H. Schwartz, and P.M. Lauren, J. Water Pollution Control Federation, 34, 1112 (1962).

56. Frasier, R.E., J. Am. Water Works Ass., 55, 624 (1963).

57. Tschopp, Ernst, and Emilia Tschapp, Helv. Chim. Acta., 15, 793 (1932).

58. Fogg, D.N., and N.T. Wilkinson, Analyst, 83, 406 (1958).

DISSOLVED GASES

The present discussion of analyses for dissolved gases in natural and waste waters is concerned only with elemental gases such as molecular nitrogen and oxygen. Anslyses for important volatile inorganic weak acids and bases, such as H_2S, CO_2, and NH_3, have been discussed in earlier sections of this chapter.

A. Separation and Concentration Techniques

Dissolved gases in waste effluents usually may be separated rather readily by vacuum degasification or by one or more of various stripping techniques. Stripping is essentially a gas-liquid extraction procedure in which an inert carrier gas is bubbled through a sample to carry off the dissolved gases for further separation, concentration, or detection. Gas transfer efficiency in such systems is dependent on the gas-liquid interfacial area and on the degree of mixing.

Gas-exchange separation can be carried out as either a batch or a continuous flow process. In one design, a continuous mixed stream of sample and carrier gas (nitrogen or hydrogen) is forced through an aspirator nozzle under fifty pounds of pressure (28). In another design, the dissolved gases are stripped from the test solution by means of multiple spinning discs rotating at high speed (26 ,33). Detection of the stripped gases in the stream of carrier gas may be done by measurement of paramagnetic susceptibility, thermal conductance, etc. (14).

The gas stripped from a wastewater sample may be separated into its various components by gas chromatography (33). Several modifications of this technique have been reported (26 ,27 ,28 , 24 ,33). By choosing appropriate detectors, it is usually possible to analyze simultaneously for almost all gases of interest in a water or wastewater sample.

B. Dissolved Oxygen

A detailed discussion of analytical methods for dissolved oxygen will serve to exemplify various techniques applicable to the analysis of most dissolved gases of interest. The analysis of dissolved oxygen in industrial wastewater has been always considered a highly significant test with respect to characterization of the physiochemical and biochemical characteristics of a waste effluent and its effect on a receiving water.

In situ analysis is probably the most effective way to analyze for dissolved oxygen. Certain precautions should be taken in cases where water samples are collected and stored for subsequent analysis. The sample must not remain in contact with air nor be agitated; either condition will cause a change in dissolved gas levels. Samples from any depth or from waters under pressure require special procedures to eliminate the effects of changes in pressure and temperature on sampling and storage. Detailed description of procedures and equipment for proper sampling of waters under prssure as well as waters at atmospheric pressure are available in the literature (2).

The time lag between a sampling and analysis is of great significance. The longer the lag, the greater the chance that the oxygen content will change because of chemical or biological activity in the test solution.

The oldest and one of the most popular methods for the analysis of dissolved oxygen is the Winkler test. Originally reported about 75 years ago, the Winkler procedure possesses most attributes of basic soundness and sensitivity. Improved by variations in equipment and techniques, and aided by modern instrumentation, this test is still the basis for the majority of titrimetric procedures for dissolved oxygen. The test is based on the quantitative oxidation of manganese (II) to manganese (IV) under alkaline conditions. This is followed by the oxidation of iodide by the manganese (IV) under acid conditions. The iodine so released is then titrated with thiosulfate in the presence of a starch indicator. The reported precision of the standard Winkler test is ±0.1 mg/l of dissolved oxygen (3).

In applying the Winkler Test for oxygen determinations in wastewaters, full consideration must be made of the interfering effects of oxidizing or reducing materials in the sample. The presence of certain oxidizing agents liberates iodine from iodide (positive interference), and the presence of certain reducing agents reduces iodine to iodide (negative interference). Reducing compounds may also inhibit the oxidation of the manganous ion. Certain organic compounds have been found to interfere with the Winkler Test in a different way. Surface-active agents for example, have been reported to hinder the settling of manganic oxide floc, thus partially obscuring the end point of the final titration with thiosulfate (14).

Several modifications of the Winkler Test have been diversed to minimize the effect of interferences found in different wastewaters. The "Alsterberger" modification (1) was developed to eliminate the effect of nitrites, which interfere with the iodometric titration as follows:

$$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + N_2O_2 + 2H_2O \qquad \text{(XII-1)}$$

$$N_2O_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2NO_2^- + 2H^+ \qquad \text{(XII-2)}$$

The nitrites formed in the reaction depicted in Equation (XII-2) oxidize more iodide ions to free iodine, thus a cyclic reaction yielding erroneously high results is established. Also, the presence of nitrites in the test solution makes it impossible to obtain a permanent end point. As soon as the blue color of the starch-iodine complex disappears, the nitrites react with more iodide to form iodine, and the blue color of the indicator appears again.

The Alsterberg modification utilizes sodium azide, which reduces the nitrites in the following manner

$$NaN_3 + H^+ \quad HN_3 + Na^+ \qquad \text{(XII-3)}$$

$$HN_3 + NO_2^- + H^+ \quad N_2 + N_2O + H_2O \qquad \text{(XII-4)}$$

The effect of a wide variety of reducing agents may be overcome by the "Rideal-Stewart" modification (22) of treating the sample with potassium permanganate solution under acid conditions. However, the difficulty in manipulation of the Rideal-Stewart modification often results in low accuracy and precision.

The alkaline hypochlorite modification (29) was designed to overcome interferences caused by sulfur compounds. Wastes from the sulfite pulp industry, for example, usually contain appreciable quantities of sulfites, thiosulfates, polythionates, etc. This procedure involves pretreatment of the sample with alkaline hypochlorite to oxidize the sulfur compounds to sulfates and sulfur. Excess hypochlorite is destroyed by potassium iodide, and the iodine is then titrated by sodium thiosulfate. Again, this modification is difficult to perform, and the results obtained are of low accuracy (14).

Suspended solids in water samples may consume certain quantities of iodine during the Winkler Test (14). This interference may be removed by flocculation with alum and ammonium hydroxide and settling of the solids prior to conducting the Winkler Test.

For samples with biological activity (e.g., activated sludge or fermentation or food processing waste effluents) the addition of copper sulfate to the sample prior to the test coagulates the biological forms. Sulfamic acid is also added to inhibit biological activity. After allowing the floc to settle, an aliquot of supernatant liquor is siphoned and analyzed for dissolved oxygen by the standard Winkler Test. The copper sulfate and the sulfamic acid are combined into a single solution in practice. This modification commonly suffers from relatively low precision (14).

The use of cerous salts in place of manganous salts have been reported to result in less interference by organic compounds (12). Attempts to minimize interferences by oxidizing agents have in-

cluded sample treatment with sodium hydroxide and ferrous ammonium sulfate (9). Oxygen in the test solution oxidizes the ferrous iron to ferric iron, which is thentitrated with ascorbic acid using 4-amino-4'-methoxydiphenylamine as an oxidation-reduction indicator.

Interferences also may be minimized by the iodine-difference modification. This method (20) involves the addition of a small quantity of iodine solution to two portions of the water, one of which serves as a control and the other of which is analyzed by the standard Winkler method. Reducing substances in the wastewater react with the iodine in both the sample and the control; therefore, the difference between the standard titration of the sample and that on the control gives an accurate value for the dissolved oxygen in the sample. It is important to maintain the same experimental conditions and time of reaction for both the sample and control after addition of the iodine solution.

Another procedure has been used to compensate for interferences present in wastewaters as well as those which might appear in the reagents ([12]). Two water sample, A and B, of equal volume are used. Sample A is analyzed by the standard Winkler Test. The order of addition of reagents to Sample B, the blank, is reversed; i.e., KOH and Kl are added first, followed by H_2SO_4 and $MnSO_4$. In the case of Sample B, dissolved oxygen is not first "fixed" by the manganous salt. Because the blank is initially made alkaline, allowance is made for substances that interfere specifically in an alkaline medium. Interfering substances in the test solution as well as those in the reagents react in both samples. Accordingly, the difference between the sample and the blank (A minus B) represents the oxygen in the sample plus the oxygen in the reagents.

If reducing substances such as sulfite are present in greater amounts than oxidants, it is possible to have a "negative" blank. In this case, identical quantities of iodine or iodate are added to both sample and blank to provide an excess of iodine after acidification. The reverse-addition method is commonly used, but it does not correct for interferences caused by ferrous iron. This leads to low results by forming ferrous hydroxide, which reacts with oxygen in the blank. The ferric ions formed do not produce an equivalent amount of iodine upon acidification.

The Winkler Test may be modified to titrate dissolved oxygen chlorometrically instead of iodometrically. The test is called "o-tolidine method." (18) After the dissolved oxygen has oxidized the divalent manganese in the conventional Winkler Test, the solution then may be acidified with chlorine-free concentrated hydrochloric acid. This reaction results in the liberation of an equivalent quantity of chlorine according to the following reaction

$$MnO_2 \cdot H_2O + 4H^+ + 4Cl^- \rightarrow Mn^{2+} + 3H_2O + 2Cl_2 \qquad \text{(XII-4)}$$

The free chlorine then reacts with orthotolidine to form the characteristic yellow-colored haloquinone chloride. The intensity of the color of the haloquinone chloride is directly proportional to the oxygen content of the sample and is measured by comparison with standards, colored slides, or by the use of absorption spectrometry. Recent studies have revealed that the intermediate chlorine is not necessary for oxidation of the orthotolidine. Colloidal manganese (IV) produced by air oxidation of manganese (II) is capable of reacting directly, even in neutral solution, with orthotolidine.

The precision and accuracy of titrimetric procedures for dissolved oxygen may be considerably improved by using better end-point detection techniques. Potentiometric detection of the iodometric end point improves sensitivity to about ± 0.001 mg/l of iodine (13) . "Dead stop" end point detection (an amperometric technique) offers an extremely sensitive as well as accurate measurement (13). The procedure is quite simple and utilizes two smooth platinum electrodes with a small potential difference (from 15 mv to 400 mv, depending on the sensitivity required). Diffusion current is measured during the course of the titration. No attempt is made to control the potential of either electrode; only the potential difference is controlled. The end point is indicated by discontinuation of current flow in the cell. As long as free iodine remains in the solution, the chief electrode reaction under the influence of the applied voltage is the oxidation of iodide to iodine at the

anode and the reverse process at the cathode. At the end point when all free iodine has been removed, the iodine to iodide reaction can no longer occur and the cell current comes to a "dead stop." Since the thiosulfate/tetrathionate reaction is highly irreversible and proceeds at only a minute rate under the influence of the applied voltage, no detectable current is observed at and beyond the end point. Ordinarily, the end point is so easily detected that there is no need for a graphical estimation of its position. By using sensitive current-measuring devices the end point can be established to an accuracy of ±0.01 microgram iodine in a 100-milliliter sample, or 1 part in 10 billion.

Coulometric titration of dissolved oxygen by in situ, electrochemical generation of iodine has been used with considerable success (9). The procedure consists of the successive additions of standard solutions of $MnSO_4$, KOH+KI, H_2SO_4, and an excess of $Na_2S_2O_3$ to the test solution. The iodine formed electrolytically reacts with the residual thiosulfate in solution. The electrolytic current is held constant by varying the potential, and the equivalence point is conveniently detected by the dead-stop end-point method.

The procedure is very accurate, to within 0.02 g/liter. It has a distinct advantage in that, because the titrant is generated in solution, errors caused in conventional titrations by contact with air are eliminated.

Direct colorimetric methods of analysis for dissolved oxygen are based on the interaction of molecular oxygen with an oxidation-reduction indicator to give a color change. One of the most commonly used indicators for the detection of oxygen in solution is methylene blue; others are indigo carmine and safranin T.

In the presence of dissolved oxygen a methylene blue solution exhibits a blue color, and in the absence of dissolved oxygen it is colorless. This indicator has been used in the relative stability test for sewage effluents (3). Quantitative colorimetric determinations of dissolved oxygen can be made with indigo carmine dyes. Indigo carmine in the reduced state reacts with oxygen to give a color change through orange, red, purple, blue, and finally a blue-green in the completely oxidized form. Colorimetric procedures are subject in general to a variety of interferences which limit their applicability to industrial wastewaters.

A radiometric procedure for monitoring dissolved oxygen is based on the quantitative oxidation of radioactive thallium-204 by oxygen in the test solution (20). Thallium-204 is primarily a beta emitter with a half-life of 3.6 years; therefore, decay over several months does not greatly reduce the sensitivity of the technique. The apparatus consists of a column of radioactive thallium electrodeposited on copper turnings, and two flow-type Geiger-Mueller counters.

The technique involves passing the test solution by one of the Geiger-Mueller counters to detect background beta-activity, then through the column where the following reaction occurs

$$4Tl + O_2 + 2H_2O \rightarrow 4Tl^+ + 4OH^- \qquad \text{(XII-5)}$$

The radioactive thallium in the effluent from the column is detected by the second Geiger-Mueller counter. One milligram of oxygen liberates 25.6×10^{-3} g of ^{204}Tl. The counting rate is directly proportional to the oxygen concentration in the test solution.

The sensitivity of the test using a column with a specific activity of 2.04 millicurie per gram of thallium is about 0.2 mg/liter. That is to say, a test solution containing 0.2 mg/l produces a ^{204}Tl counting rate equal to the background counting rate of the detector. As a rule, because of the randomness of radioactive disintegrations, the precision of this method is ±2%. It is important to note that oxidizing agents and changes in the pH of the test solution may interfere with the test.

A few coulometric methods of analysis for dissolved oxygen have been reported. For purposes of orientation, it is helpful to note that air-saturated water at 25°C and under 750 mm Hg air pressure contains 8.18 mg of dissolved oxygen per liter. This in terms of coulometric response is 0.1083 amp.sec/g, a rather large quantity. Two coulometric procedures are discussed here (4,14). In one method of deoxygenated solution of chromic ions is added to the water sample. During the test, chromous ions are generated electrolytically and are then reoxidized by the oxygen in solution. The apparatus immediately detects any excess of chromous ions, marking

the end of the titration. This method is sensitive to 0.3 mg dissolved oxygen per liter and has an accuracy of ±2%.

Another coulometric method is based on the interaction between oxygen and an ammonia-copper complex $Cu(NH_3)_2^+$. This is followed by the reduction of the oxidized ammonia-copper complex $Cu(NH_3)_2^+$ on a platinum cathode. The amount of current used is equivalent to the oxygen concentration in the test solution.

Use of a constant-potential derivative coulometric system was reported recently (8). The working electrode was composed of tiny metal spheres packed in a ceramic tube. No field experience has been reported with this system, however.

Voltammetric analyses for dissolved oxygen in wastewaters have been carried out with various degrees of success using rotating platinum electrodes and dropping mercury electrodes. The main difficulty in using such electrode systems in industrial waste effluents is the presence of surface active and electroactive interferences which frequently cause "electrode poisoning." A detailed discussion of the effects of surface active agents on the polarographic oxygen determination is available in the literature (15).

Various modifications of the dropping mercury electrode system have been developed for continuous monitoring of dissolved oxygen (15,31). In the absence of interferences, the sensitivity of this technique ranges from 0.05 to 0.10 mg of dissolved oxygen per liter.

Oxygen sensitive galvanic cells have been used for some time for analyses of water effluents (15). These are made of galvanic couples of an inert metal cathods (e.g., lead, zinc or antimony)(30). The cathodic reduction of molecular oxygen results in a galvanic current proportional to the concentration of dissolved oxygen in the test solution. Changes in the pH and the conductivity of the test solution influence the oxygen measurement.

Voltammetric Membrane Electrode Systems-Oxygen Measurement by Membrane Electrode Systems

Principle of Oxygen-Membrane Electrodes: There are three main steps involved in the operation of oxygen membrane electrodes. The first is the permeation of molecular oxygen from the test solution through the plastic membrane layer. The second is the permeation of molecular oxygen through the electrolyte solution layer. The third step is the electrolytic discharge of oxygen on the silver cathode, with the subsequent generation of an equivalent quantity of current.

To aid in understanding of the theory involved, the diffusion current equations as reported by the senior author (16) are presented briefly. Figure XII-1 shows a cross-sectional diagram normal to the surface of the indicator electrode, which is composed of an electrolyte solution layer of thickness"A" and a membrane layer of thickness "B." Concentration profiles at different times of electrolysis, t, are also shown in Figure XII-1.

Figure XII-3 shows the corresponding current-time curve, in which steady-state operation was reached after 90 seconds. The current is assumed to be solely dependent on the rate of mass transfer (linear finite diffusion) of reactants to the electrode surface and not on the overall charge-transfer rate or on the kinetics of a chemical reaction coupled with the charge-transfer process. As soon as the electrolysis circuit is closed, the current shoots up to a high initial value, which is characteristic of charging the capacitance of the double layer (Figure XII-2) after which the current decreases in a manner determined by the rate of mass transport, as illustrated by the concentration profiles in Figure XII-1. Current measurements at t=10 seconds, corrected for capacitance current thus depends on the concentration of the electroactive species in the electrolyte solution layer only. This can be easily seen on considering the diffusion current equation for such two-film (the electrolyte film and

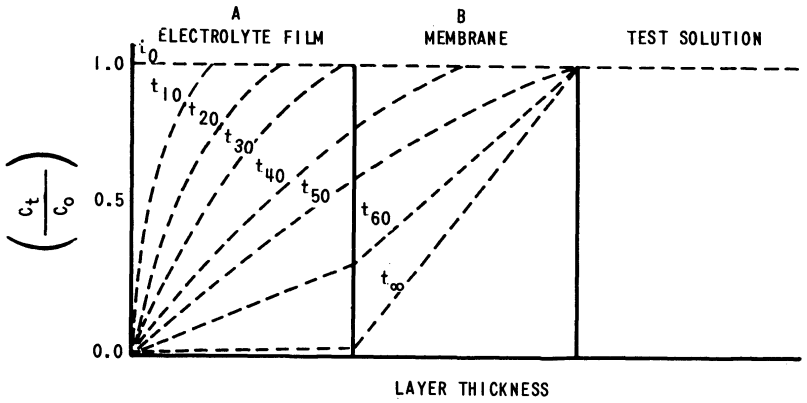


Figure XII-1. CONCENTRATION PROFILES

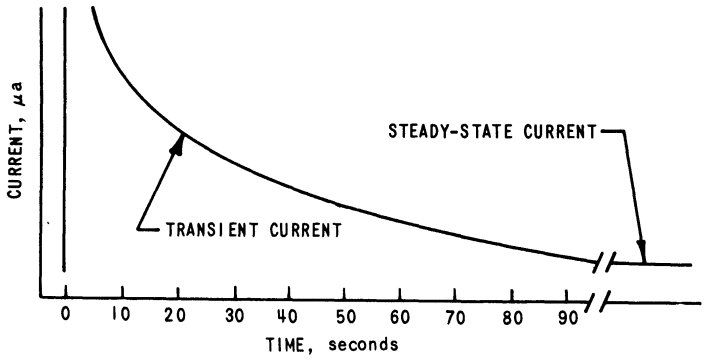


Figure XII-2. CURRENT-TIME CURVE

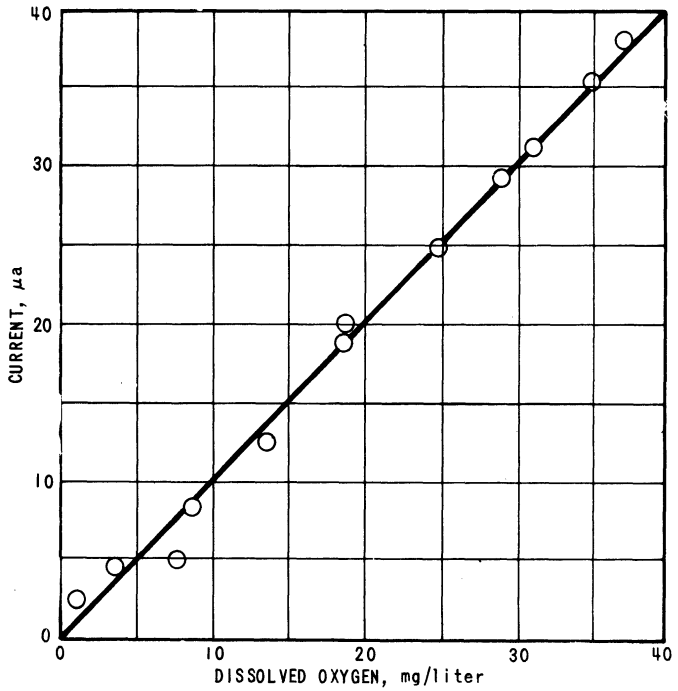


Figure XII-3. CALIBRATION CURVE AT 25°C

the membrane) electrode systems. At very small values of t (e.g., below 30 seconds in Figure XII-2), the electrolyte film is of primary importance and the current varies according to the following equation

$$i_t = nFA\left(\frac{D_f}{t}\right)^{0.5} C\left[1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2A^2}{D_f t}}\right] \qquad \text{(XII-1)}$$

where i_t is the current at time t, μa; n is the number of electrons exchanged per mole of reactant; F equals Faraday equals 96,600 coulombs; $\bar{a}$ is the surface area of indicator electrode, cm^2; D_f is the diffusion coefficient of the reactant in the electrolyte solution layer, cm^2/sec; t is time, sec; C is concentration (strictly the activity) of reactant species in test solution, M/cm^3; A is the thickness of the electrolyte solution film, cm.

At very small t values, the summation term in Equation (XII-1) can be neglected and the current varies inversely with the square root of time.

$$i_t = \left[nF\bar{a}\left(\frac{D_f}{\pi}\right)^{0.5} C\right] t^{-0.5} \qquad \text{(XII-2)}$$

At larger values of t($t \geq 30$ sec in Figure XII-1), diffusion in the membrane is governing.

$$i_t = nF\bar{a}\,\frac{P_m}{B}\,C\left[1 + 2\sum_{n=0}^{\infty} e^{-\frac{n^2\ {}^2D_m t}{B^2}}\right] \qquad \text{(XII-3)}$$

where P_m is the membrane permeability coefficient, cm^2/sec; D_m is the diffusion coefficient of reactant in film, cm^2/sec. At large values of t (above 90 sec), steady-state conditions are achieved and Equation (XII-3) is then

$$i_{\infty} = nF\bar{a}\frac{P_m}{B}C \qquad \text{(XII-4)}$$

The rate determinant in this case is the transport through the membrane. Accordingly, the generated current is directly proportional to the rate of permeation of molecular oxygen through a given membrane, which, in turn, is directly proportional to the DO content of the test solution. A typical calibration curve showing the linearity of response under steady-state conditions is shown in Figure XII-3.

Unpublished data from recent studies by the senior author revealed that after the first day of continuous operation, the electrode reactions of the galvanic cell oxygen analyzer are partially as follows

Cathodic reaction

$$\tfrac{1}{2}O_2 + H_2O + 2e \longrightarrow 2OH^- \qquad \text{(XII-5)}$$

Anodic reaction

$$Pb + 2OH^- \longrightarrow PbO + H_2O + 2e \qquad \text{(XII-6)}$$

Overall reaction

$$Pb + \tfrac{1}{2}O_2 \longrightarrow PbO \qquad \text{(XII-7)}$$

It is evident then that as the cell discharges, there is no net concumption of the OH^- concentration. Although, the OH ions are not consumed in the overall cell reaction, they are required to sustain the anodic reaction. Hence, there will be a localized defficiency of OH^- ions at the anode and an increase in the OH^- ions in the electrolyte solution layer from the central cathodic area toward the peripheral anode.

Oxygen membrane electrodes have three main components: the membrane, the oxygen-sensing element, and the electrolyte solution. The membrane, the unique feature in such electrode systems, serves

in three different capacities. First, the membrane acts as a protective diffusion barrier separating the sensing element from the test solution. Since plastic membranes are permeable to gases only, oxygen molecules pass through, but electroactive and surface-active contaminants present do not. The possibility of poisoning the sensing element is thus eliminated.

Second, the membrane serves to hold the supporting electrolyte in contact with the electrode system and thus makes it possible to determine oxygen in gaseous samples as well as in nonaqueous solutions such as industrial wastes (16).

The third advantage, discussed previously, is that the membrane constitutes a finite diffusion layer, the thickness of which is independent of the hydrodynamic properties of the test solution.

Membranes must meet the following requirements. Primarily, the membrane should have excellent permeability to oxygen, yet be practically impermeable to ionic species and water molecules from the test solution. Its permeability characteristics should not change with time, and there should be no intereaction between the membrane material and the diffusion oxygen molecules or ionic species present in the test solution. The membrane should be able to withstand slight amounts of stretching without breaking so that it can be applied easily to the electrode surface.

Polyethylene, Teflon, polypropylene, and synthetic rubber show good permeability for oxygen. Polyethylene membranes of low crystallinity were found to have high permeability to oxygen.

As far as the oxygen-sensing element is concerned, platinum has been used extensively as cathode material in electrochemical analysis for DO. Silver and gold are, however, better cathode materials for oxygen detection than the conventionally used platinum. The reduction of oxygen on a platinum cathode was found to be a complicated process since the reaction proceeds through the formation of a platinum oxide layer. Significantly, this step does not occur with silver or gold electrodes.

The electrolyte solution in membrane electrode systems should be a highly conducting aqueous solution that does not interact with the electrode material. In voltammetric systems the type and concentration of the electrolyte solution are dictated by the reference

anode, e.g., for an Ag/AgCl reference electrode, a 3% KCl solution is used.

Sensitivity -- The membrane oxygen electrode is commonly calibrated by means of the Winkler Test. A typical calibration curve is given in Figure XII-3, which shows a linear response to oxygen from zero to saturation values.

A basic operational requirement for membrane electrode systems is the maintenance of a threshold amount of mixing in the test solution around the tip of the analyzer. This can be achieved either by driving the solution past the surface of the analyzer by means of a pump or a stirring device, or by moving the analyzer. In the laboratory, a magnetic stirrer or a motor-driven glass stirrer is usually used. Since the flow past the probe must be not less than 1 ft/sec, appropriate flow in the field may be attained by the natural flow of the water, by towing the prove behind a moving boat, or by moving the probe up and down manually. Attachments containing battery-driven small propellers (10) may be mounted on the tip of the probe.

The effect of stirring the test sample on instrument sensitivity is shown in Figure XII-4. From an initial low value with no stirring, the sensitivity rises rapidly with increasing stirring speed and then assumes a steady value. Adequate stirring of the test solution is necessary so that the oxygen concentration at the membrane surface will be equal to that in the bulk of the solution. Only under such conditions will the measured diffusion current be directly proportional to the oxygen concentration in the bulk of the test sample.

Temperature Coefficient -- Another critical characteristic of voltammetric membrane electrodes is the relatively high temperature coefficient, which is largely due to the effect of temperature changes on the permeability characteristics of the plastic membrane. Temperature effects on the electrode reaction kinetics or the electrode potential are relatively negligible. Calibration curves for one of the galvanic cell oxygen analyzers over the temperature range from 5^{o} to 35^{o}C are shown in Figure XII-5.

The instrument sensitivity, ϕ, was found to vary with temperature (Figure XII-5).

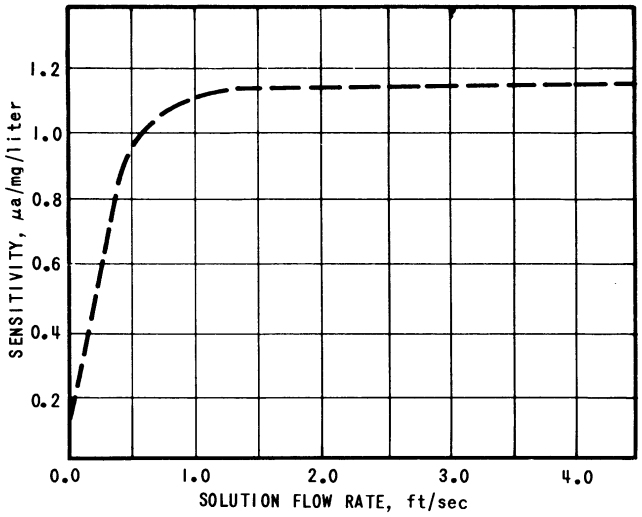


Figure XII-4. EFFECT OF STIRRING ON SENSITIVITY

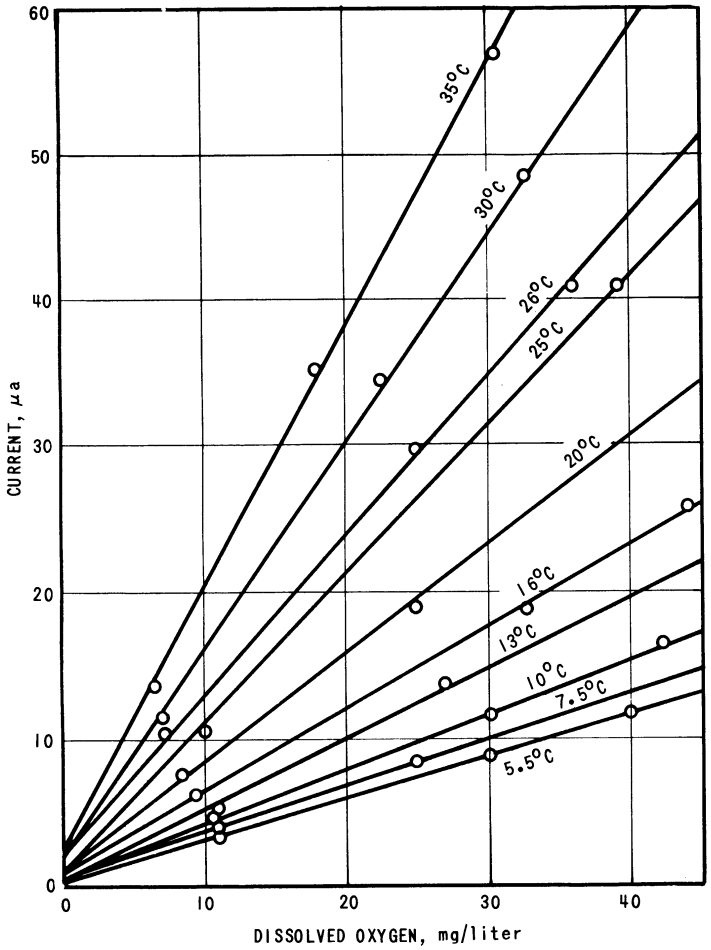


Figure XII-5. CALIBRATION CURVES FOR DIFFERENT TEMPERATURES

$$\frac{d\phi}{dT} = m^o \frac{\phi}{T^2} \qquad \text{(XII-8)}$$

where ϕ is the sensitivity, μa/mg/liter; T is the temperature, ^oK; m^o is the temperature coefficient, ^oK.

If log ϕ is plotted versus 1/T, a straight line is obtained.

$$\log \phi = \log \phi_o + \frac{-m^o}{2.303} \left(\frac{1}{T_o} - \frac{1}{T}\right) \qquad \text{(XII-9)}$$

in which $-m^o/2.303$ is the slope and b is the ordinate intercept. If m^o is determined, the instrument sensitivity can be calculated for any desired temperature.

$$\log \phi = \log \phi_o + \frac{m^o}{2.303} \left(\frac{1}{T_o} - \frac{1}{T}\right) \qquad \text{(XII-10)}$$

Nomograph charts also can be constructed for the temperature correction.

Temperature compensation can be done automatically by incorporating a thermistor setting in the electrode circuit. Thermistors do not compensate fully for the temperature errors to less than ±10% of the reading over the temperature range of 5^o to 35^oC, or less than ±5% over the 15^o to 45^oC range (4). When high accuracy is required, calibrated nomographic charts should be used.

Application -- Interpretation of the results of oxygen membrane electrode systems requires careful consideration. It is helpful to point out the similarity between the glass membrane electrodes, used for the measurement of pH and pNa, and oxygen membrane electrodes. The measured parameter in the glass electrode system is an asymmetry potential across the glass membrane. This potential across the glass membrane is related to the hydrogen ion activity in the test solution.

In the case of oxygen membrane electrode systems, the measured diffusion current is solely dependent on the difference in the chemical potential of the electroactive species across the membrane. One should expect then that as glass electrodes are used for pH determinations (intensity), oxygen membrane electrode systems will likewise measure an "intensity property" that is essentially equivalent to the activity of molecular oxygen in solution. This should be differentiated from "extensive parameters" as determined by titrimetric methods such as the Winkler Test. Accordingly, the difference between the pH value determined by the glass electrode and acidity as determined by titration with a standard base is essentially the same as the difference between oxygen analysis by a membrane electrode and the Winkler Test. Only under ideal conditions and in the absence of certain impurities are diffusion current values from membrane electrode systems proportional to concentration. The correct form of the diffusion current equation for membrane electrodes is

$$i = \left(nF\bar{a}\,\frac{P_m}{B}\right) a = \phi_a\, a = \phi_a\, \gamma C \qquad \text{(XII-11)}$$

where ϕ_a is the sensitivity coefficient with respect to activity, $\mu a/M/cm^3$; γ is the activity coefficient of molecular oxygen; n is the number of electrons exchange per mole of reactant; F is Faraday equals 96,500 coulombs, $\bar{a}$ is the surface area of the indicator electrode, cm^2; B is the thickness of the membrane layer, cm; P_m is the membrane permeability coefficient, cm^2/sec; a is the activity of the molecular oxygen, M/cm^3; C is the concentration of molecular oxygen, M/cm^3.

The dependence of the diffusion current on the ionic strength of the test solution (Figure XII-7) can be expressed as follows

$$i = (e^{K_s I}\, \phi_a)\, C \qquad \text{(XII-12)}$$

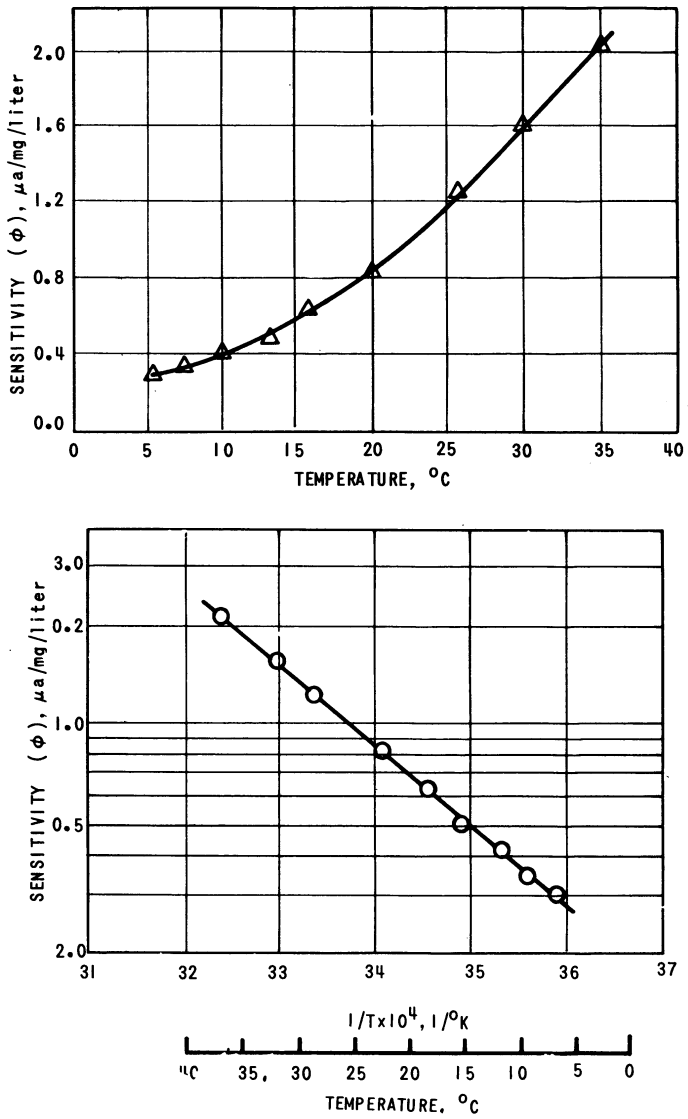


Figure XII-6. EFFECT OF TEMPERATURE ON SENSITIVITY

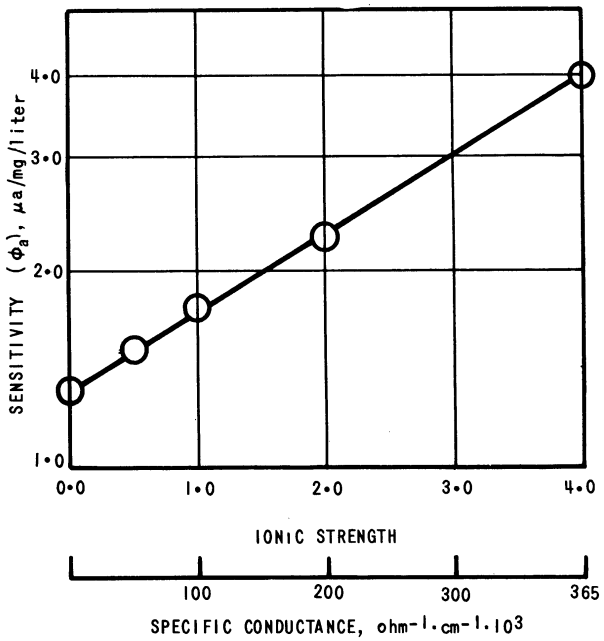


Figure XII-7. EFFECT OF IONIC STRENGTH ON SENSITIVITY

where K_s is the salting-out coefficient; I is the ionic strength.

Equation (XII-12) correlates the diffusion current, i, to the concentration of molecular oxygen in the test solution as a function of the ionic strength, I. In the case that I = 0, e.g., distilled water, then the term $e^{K_s I}$ will be unity and Equation (XII-12) will be equal to Equation (XII-11). By means of Equations (XII-11) and (XII-12) values can be determined for the activity coefficient, γ, and the salting-out coefficient, K_s, in salt solutions (e.g., KCl, $CaCl_2$, Na_2SO_4), which are of high theoretical significance.

Recent investifations have shown that simple methods can be developed to compensate for the temperature and the salt effects on the determination DO concentration by membrane electrodes.

The temperature effect can be described as follows

$$i = \phi_{o,t}\, e^{-\frac{E_p}{R}\,\Delta\,\frac{1}{T}}\, C \qquad \text{(XII-13)}$$

where $\phi_{o,t}$ is the sensitivity (current in ampheres/DO concentration in M/liter) at a reference state with respect to temperature in ^oC; E_p is the activation energy of the permeation of the membrane, cal/M; T is the temperature, ^oK; R is the gas constant, cal/M/^oK; C is the concentration of molecular oxygen, M/liter.

Similarly the effect of the salt content of the test solution can be expressed as follows

$$i = \phi_{o,s}\, e^{K_s \Delta I}\, C \qquad \text{(XII-14)}$$

where $\phi_{o,s}$ is the sensitivity at a reference state with respect to the ionic strength of the test solution, amp/M/liter.

The ionic strength of the test solution can be determined accurately for any given water by means of conductance measurements, as shown by the following equation

$$L = \theta + (\lambda I) + (\delta I^2) + (\Gamma' I^3) \qquad \text{(XII-15)}$$

where L is the specific conductance, $ohm^{-1}cm^{-1}$; θ, λ, δ, and Γ are constants.

The nonlinear relationship given in Equation (XII-15) can be approximated, however, to

$$\Delta L = K_i \Delta I \qquad \text{(XII-16}$$

where K_i is the proportionality constant.

Equation (XII-16) indicates the linear dependence of conductance on ionic strength, which holds in most surface waters, including estuarine water, but does not hold in certain industrial wastes of high salt content.

By combining Equations (XII-14) and (XII-16), it follows that

$$i = \phi_{o,s} e^{K_s \Delta L} C \qquad \text{(XII-17)}$$

where K_s equals $K_s K_i$.

The exponential terms in Equations (XII-13) and (XII-17) express the effect of the temperature and salt content.

Membrane electrode systems offer the following advantages.

1. The activity (and concentration) of molecular oxygen can be determined by using membrane electrode systems. Activity determinations are highly significant whenever environmental measurements and biochemical systems are concerned.

2. Since the sensing element is separated from the test solution by a selective permeable membrane, it is possible to analyze for DO in solutions containing ionic and organic contaminants.

3. The membrane serves as a diffusion layer, the thickness of which is independent of the hydrodynamic properties of the test solution. Accordingly, membrane electrodes exhibit more stable performance characteristics in flowing solutions than conventional electrode systems.

4. Membrane electrode systems possess the unique ability of analysis for DO in aqueous, nonaqueous, and gaseous systems.

5. One of the main advantages of membrane electrode systems is their suitability for field use. Because of their ruggedness, portability, and ease of operation and maintenance, they are ideal instruments for the analysis of DO under adverse environmental conditions.

6. Being completely submersible, they can be used to analyze for DO in situ.

7. Like other electrochemical systems, membrane electrodes can be used for continuous monitoring.

A DO determination by means of membrane electrodes is a relatively simple procedure; however, certain difficulties are sometimes encountered.

1. Most of the difficulties associated with these electrode systems are mainly caused by a lack of understanding of the procedure and principle of operation. In polarography, the electrode surface is continuously renewed, but in membrane electrode systems this is not the case. Great care should be taken during the recharging of the electrode system to avoid contaminating the sensing element.

2. Improper mounting of the membrane might lead to trapping small air bubbles under the membrane. The bubbles cause a slower response to oxygen and a higher residual current.

3. Insufficient flow across the membrane surface results in erratic response; maintaining a threshold mixing value in the test solution is therefore essential.

4. Plastic membranes show selective permeability to various gases and vapors. Gases reduced at the potential of the sensing electrode, e.g., SO_2 and halogens, cause erroneous readings, but in aqueous systems these gases rarely exist in a free state. Other gases capable of permeating the plastic membrane may contaminate the sensing electrode of react with the supporting electrolyte, e.g., CO_2 and H_2S.

Oxygen membrane electrodes have been used in a variety of applications in the environmental sciences and engineering. Typical applications are oxygen monitoring in rivers and lakes, aeration studies, and oxygen utilization of domestic sewage (15 , 17 ,31). Other applications include continuous DO recording in activated-sludge processes (24), in respiration studies as a replacement of the Warburg Apparatus (12) in oceanographic studies (5 , 6), and in fermentation studies (22).

REFERENCES

1) Alsterberg, G., Biochem. J., 159, 36 (1925).

2) American Society of Testing Material, "Manual on Industrial Water and Industrial Waste Water," American Society for Testing Materials, 2nd ed., (1964).

3) APHA, AWWA and WPCF, "Standard Methods - Water and Wastewater," American Public Health Ass., 12th ed. (1965).

4) Barbi, G., and S. Sandroni, Com. Nazl. Energia Nucleare, CNI-55, 3 (1960).

5) The Beckman Laboratory Oxygen Sensor. Bulletin 7013. Beckman Instruments, Inc. Fullerton, California.

6) Cassie, R. M. Calibration and operation of dissolved oxygen electrode. New Zealand Oceanographic Institute. 1963.

7) Duxbury, A. C. Calibration and use of a galvanic type oxygen electrode in field work. Limnol. and Oceanography. 8:483. 1963.

8) Eckfeldt, E. L., and E. W. Shaffer, Anal. Chem., 36, 2008 (1964).

9) Erdey, L., and F. Szabadvary, Acta. Chem. Acad. Sci., Hungary, 4, 325 (1954).

10) Hissel, J., and J. Price, Bull. Centre Belge Etude et Document Eaux, 44, 76 (1959).

11) Jarrel Ash Company. Dissolved oxygen analyzer. Special Bulletin. Boston, Mass. 1962.

12) Lederer, V. V., Chem. Listy, 41, 230 (1947).

13) Loomis, W. F. Rapid microcolorimetric determination of dissolved oxygen. Anal. Chem. 26:402. 1954.

14) Mancy, K. H., and T. Jaffe, Environmental Health Series, Public Health Service Publication, 999-WP-37 (1966).

15) Mancy, K.H., and D. A. Okun, Anal. Chem., 32, 108 (1960)

16) Mancy, K. H. and D. A. Okun. Oxygen in waste treatment - the galvanic cell oxygen analyzer. special report to NIH, Dept. of Environmental Sciences and Engineering, School of Public Health University of North Carolina, Chapel Hill, N.C. 1961.

17) Mancy, K. H., D. A. Okun, and C. N. Reilly. The galvanic cell oxygen analyzer. J. Electroanal. Chem. 4:65. 1962.

18) Mancy, K. H., and W. C. Westgarth. A galvanic cell oxygen analyzer, JWPCF. 34:1037. 1962.

19) Meyer, H. J., and C. Brack, Chem. Eng. Tech., 22, 545 (1950).

20) Potter, E. C., and J. F. Moresky, "The Use of Cation-Exchange Resin in the Determination of Copper and Iron Dissolved at Very Low Concentrations in Water," in Ion Exchange and Its Applications, Society of Chemical Industry, London, p. 93 (1955).

21) Richter, H. G., and A. S. Gillespie, Jr., Anal. Chem., 34, 1116 (1962).

22) Rideal, S., and G. Stewart, Analyst, 26, 141 (1901).

23) Strohm, J. D., and R. F. Dale. Dissolved oxygen measurement in yeast propagation. Ind. Eng. Chem. 53:760. 1961.

24) Sullivan, J. P., "Determination of Dissolved Oxygen and Nitrogen in Sea Water by Gas Chromatography," Marine Science Department, Report No. 0-17-63, U. S. Naval Oceanographic Office, Washington 25, D.C. (1963).

25) Sulzer, F., and W. M. Westgarth. Continuous DO recording in activated sludge. Water and Sewage Works. 8:266. Oct. 1962.

26) Swinnerton, J. W., V. J. Linnenbom, and C. H. Cheek, Anal. Chem., 34, 483 (1962).

27) Szekely, G., G. Raoz, and G. Traply, Period. Polytech., Chem. Engr., 10, 231 (1966); Chem. Abstracts, 67, 500 (1967).

28) Thayer, L. C., and D. A. Robinson, Proc. First International Congress of Instrument Society of America, Philadelphia, 9, 2 (1954).

29) Theriault, E. G., and P. D. McNamee, Ind. Engr. Chem., 4, 59 (1932).

30) Todt, F., and R. Freier, Ger. Pat. 1-012-764 (1957).

31) Tyler, C. P., and J. H. Karchmer, Anal. Chem., 31, 499 (1959).

32) Weiss, C. M., and R. T. Oglesby. Instrumentation for monitoring water quality in reservoirs. Presented at 83rd Annual Conference of AWWA, May 23, 1963.

33) Wilson, R. F., Limnol. Oceanog., 6, 259 (1961).