

TN-101

INSTRUMENTATION FOR WATER QUALITY



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## PREFACE

The rapid development of sophisticated instrumentation coupled with concern over trace quantities of individual constituents has resulted in the application of procedures using such instrumentation for the analysis of natural and wastewaters. In large part it is the development of such instruments followed by their application to environmental analysis that has led to the present interest in the analysis of trace quantities of specific constituents. The various techniques included in this report are flame photometry, ion selective electrodes, total organic carbon analyser and atomic absorption spectrometry. Emphasis has also been given on conventional instruments like pH meter, turbidity meter, etc., with a view to increase their performance and reproducibility. This report describing various aspects of instrumental analysis, should prove useful for scientists and technologists engaged in water quality monitoring.

The present report has been prepared by Dr. C. K. Jain, Scientist, and is a part of training which he obtained at International Institute for Hydraulic and Environmental Research, Delft, The Netherlands, within the framework of Indo-Dutch Training Programme on Water Management (WAMATRA Phase-II).

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## 1.0 pH METER

### 1.1 General

The pH value is a measure of hydrogen ion concentration. For most practical purposes the pH of an aqueous solution can be taken as the decadic logarithm of the reciprocal of the hydrogen ion concentration (more precisely, of the hydrogen ion activity) in moles per litre. The practical pH scale extends from 0 (very acidic) to 14 (very alkaline) with the middle value of 7 corresponding to exact neutrality at 25°C

The pH value of natural water is an important index of acidity or alkalinity and is usually governed by the carbon dioxide/bicarbonate/carbonate equilibria and lies in the range between 4.5 and 8.5. This correlation in turn depends substantially on the intensity of the process of photosynthesis and the biochemical oxidation of organic substances as well as chemical conversions of some mineral substances.

The effect of pH on the chemical and biological properties of liquids makes its determination very important, e.g. for controlling corrosion and for control of water or waste treatment processes. The pH value is used in several calculations in analytical work and its adjustment is necessary for some analytical procedures.

The pH value of water may be determined potentiometrically by a wide variety of pH meters. They are equipped with glass and reference electrodes which require standardizing with standard buffer solutions before each measurement.

## 1.2 Principle

The basic principle of pH measurement is determination of hydrogen ion activity by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kpa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode is commonly used.

The sensor electrode (glass electrode) is a bulb of special glass containing a fixed concentration of HCl or a buffered chloride solution in contact with an internal reference electrode. Upon immersion of a new electrode in a solution the outer bulb surface becomes hydrated and exchange sodium ions for hydrogen ions to build up a surface layer of hydrogen ions. This, together with the repulsion of anions by fixed, negatively charged silicate sites, produces at the glass-solution interface a potential that is a function of hydrogen ion activity in solution.

## 1.3 Interferences

The glass electrode is relative immune from interference by colour, turbidity, free chlorine, oxidants or reductants, as well as from high salinity.

The error caused by high sodium-ion concentrations at a pH above 10 may be reduced by using special 'low-sodium-error' electrodes.

Temperature effects the potential of electrodes and the ionization in the sample. The first effect can be compensated for

by a resistance thermometer immersed in the test solution and connected to the electrical circuit of the pH meter. Many pH meters are equipped with both manual and automatic temperature compensation. The second effect is inherent in the sample and is taken into consideration by recording both the temperature and the pH of each sample.

An adequate level of filling solution should be ensured in the reference electrode and no air bubble should be trapped in the solution or in the liquid junction

#### 1.4 Instrument Description

pH meter : Both mains and battery operated model are available, the latter type can be used for field measurement. For most purposes reporting pH value to 0.1 pH is adequate.

Glass electrode : This must be compatible with the pH meter used and must be suitable for the particular application. Special electrodes are available for pH values greater than 10, and for temperature greater than 60°C. Combined glass/reference electrodes are also available and are convenient to use.

Reference electrode : The mercury/calomel electrode is widely used but the silver/silver chloride electrode may be preferable because it gives more reproducible and more reliable results.

#### 1.5 Procedure

Standardize the pH meter according to the manufacturer's instructions with a frequency depending on the accuracy desired and on the stability of the instrument but not less than once a day. Choose a standard buffer solution with a pH



value close to that of the water to be tested. Measure the temperature of the buffer solution. If manual temperature compensation is employed, set the temperature control to the temperature of the buffer. Using the buffer adjustment, set the meter to the pH of the buffer at that temperature. Check the electrode response occasionally by measuring a second standard buffer solution of different pH. When the error becomes too great discard the electrode. Some pH meters can correct for nontheoretical response with an electrode slope compensator. (Theoretical response is 59.16 mV per pH unit at 25°C but on ageing the response becomes less than this.)

Before measuring the pH of the test sample, wash the electrodes thoroughly first with distilled water and then with the sample. Set the temperature control to the temperature of the sample, if manual compensation is used. Allow the system to stabilize before making the final reading. A duplicate measurement should be made.

Make determinations in unstirred solutions to avoid the loss of carbon dioxide or other volatile components which would alter pH values.

Between measurements, the electrodes are kept in distilled water. New or dried-out glass electrodes should be prepared for use by soaking in 0.1 N hydrochloric acid for eight hours or according to the maker's instructions.

## 2.0 DISSOLVED OXYGEN METER

### 2.1 General

Dissolved oxygen content of water depends on the physical, chemical and biochemical activities in the water body and also on the atmospheric pressure and temperature. The oxygen content of the water body is an important indicator of its purity. Adequate dissolved oxygen is necessary for fish and other aquatic organisms. It is also directly connected with its chemical content (dissolved solids - salinity), biological, microbiological activity, total organic content and photosynthetic activity. Hence, quite often it becomes essential to measure continuously dissolved oxygen content of water streams to keep a constant check on its pollution due to sewage or industrial waste discharge.

There are basically three methods for dissolved oxygen measurement. They are i) Winkler or iodometric method and its modifications, ii) polarographic method, and iii) electrometric method using membrane electrodes.

The first method which involves iodometric titration is time consuming and is not applicable to a variety of industrial and domestic waste waters. Moreover, the iodometric method is not suited for field testing and cannot be adapted easily for continuous monitoring. The polarographic method although quite sensitive but is not always reliable since its electrode is badly poisoned by the impurities present in the sample.

The membrane electrodes provide an excellent method for DO analysis in polluted waters, coloured waters and waste

effluents. Sensing element of the electrode system is protected by an oxygen permeable membrane that serves as a diffusion barrier against impurities making them suitable for in-situ measurements. Their portability and ease of operation make them convenient for field applications.

## 2.2 Principle

Oxygen sensitive membrane electrode composed of two solid metal electrodes in contact with supporting electrolyte separated from the test solution by a selective membrane. This membrane retains water and dissolved solids almost completely, but allow oxygen and other gases to pass through. Under the influence of a potential metal ions enter the solution at the anode, electrons pass from anode to cathode, and oxygen is reduced at the cathode. The hydroxyl ions react with the metal ions at the surface of the anode.

The steady state diffusion current thus developed is linearly proportional to the concentration of molecular oxygen at a fixed temperature.

## 2.3 Interference

Plastic films used with membrane electrode system are permeable to a variety of gases besides oxygen, although none is depolarised easily at the indicator electrode. Prolonged use of membrane electrodes in water containing such gases as hydrogen sulfide tends to lower cell sensitivity.

## 2.4 Instrument Description

Dissolved oxygen meter consists of a sensor - the membrane probe, electronic amplifier and suitable measuring

device. A typical membrane probe consists of two metallic electrodes embeded in epoxy. A small space between the electrodes is filled with a suitable electrolyte and a thin membrane made up of polyethylene or teflan, which is permeable for oxygen is stretched across the end of the sensor isolating the electrodes from the actual sample. The measuring device for the output from dissolved oxygen probes is normally calibrated in convenient scale (0 to 10, 0 to 15, 0 to 20 mg/L) with a sensitivity of approximately 0.05 mg/L.

## 2.5 Procedure

A calibration mark on the meter is set against a known oxygen value. Air saturated water may be prepared by stirring distilled water with a stirrer at a constant temperature untill the concentration of dissolved oxygen reaches a constant value. Stirring should be rapid but not so vigorous that air bubbles are entrained

The electrode is immersed in a sample which has been deoxygenated by an excess of sodium sulphite in the presence of a trace of cobalt ion and zero oxygen reading is noted.

Place the probe in the sample to be measured and allow sufficient time for probe to stabilize to sample temperature and dissolved oxygen. Read dissolved oxygen from the meter.

### 3.0 TURBIDITY METER

#### 3.1 General

Turbidity is one of the basic characteristics of water such as colour, odour and potability. It is caused by suspended matters, such as clay, silt, finely divided organic and inorganic matter, soluble coloured organic compounds, and plankton and other microscopic organisms like algae, bacteria and planktons. The turbidity being connected with potability of water directly, indirectly or aesthetically, its measurement is very important in deciding the quality of water samples.

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. Correlation of turbidity with the weight concentration of suspended matter is difficult because the size, shape, and refractive index of the particulates also affect the light scattering properties of the suspension.

The standard method for the determination of turbidity has been based on the Jackson candle turbidimeter, however the lowest turbidity value that can be measured directly on this instrument is 25 units.

Most commercial turbidimeters available for measuring low turbidities give comparatively good indications of the intensity of light scattered in one particular direction, predominantly at right angles to the incident light. These nephelometers are unaffected relatively by small changes in design parameters and therefore are specified as the standard instruments for measurement of low turbidities. Its greater

precision, sensitivity and applicability over a wide turbidity range make the nephelometric method preferable to visual methods.

### 3.2 Principle

This method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same condition.

In this method light beam enters the sample through the bottom of the sample cell and passes up through the sample and into the light shield whose black interior acts as a light trap to help minimize stray light (Figure 1). As the light passes through the sample, some light is scattered by turbidity in the sample. A portion of that light scattered at 90 degrees is sensed by the photocell and the resulting photocell output is conditioned to drive the instrument meter. The meter scale is calibrated in nephelometric turbidity units to provide direct turbidity readouts

### 3.3 Interference

Rapidly settling coarse sediments, air bubbles and dissolved substances that absorb light are the prime source of interference.

### 3.4 Instrument Description

Turbidimeter consists of a nephelometer with a light source for illuminating the sample and one or more photoelectric detectors with a readout device to indicate intensity of light scattered at 90°C to the path of incident light.

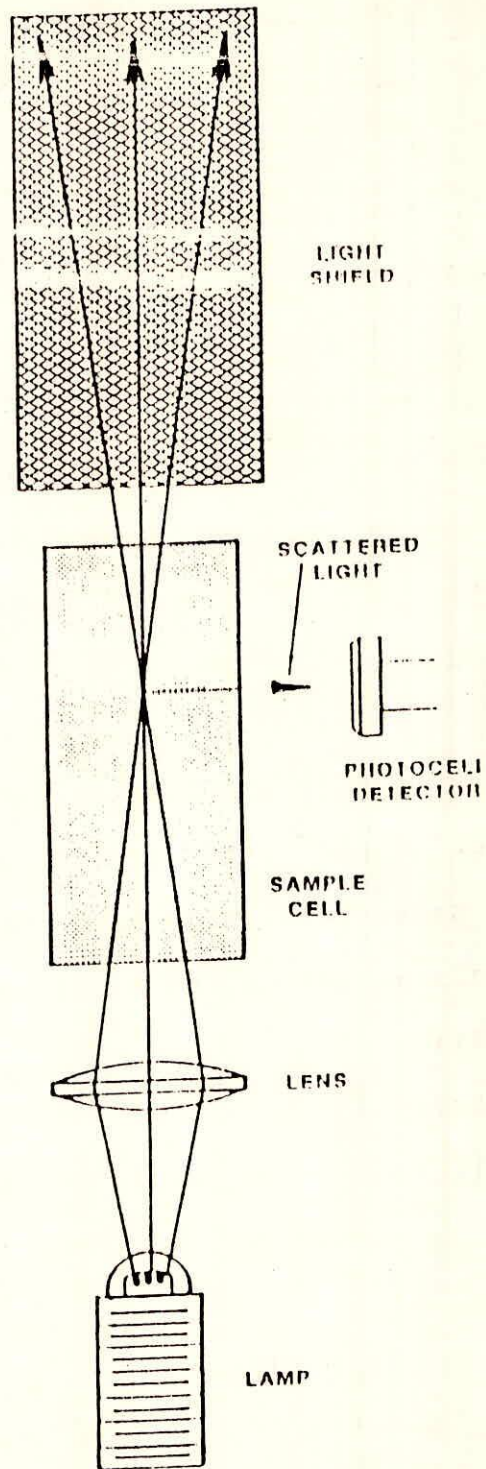


FIGURE 1: LIGHT PATH DIAGRAM

### 3.5 Procedure

Follow the manufacturer's operating instructions for calibration of the instrument. Thoroughly shake sample, wait until air bubbles disappear and pour sample into turbidity meter tube.

Read turbidity directly from instrument scale or from appropriate calibration curve. For high turbid samples, dilute sample with one or more volume of turbidity free water. compute turbidity of original sample from turbidity of diluted sample and the dilution factor.



## 4.0 FLAME PHOTOMETER

### 4.1 General

Flame photometry offers excellent possibilities for the development of analytical procedures for those metallic ions which can be excited by the relatively low excitation levels available in the flame. Interest in quantitative procedures has increased rapidly in the past few years. This has been mostly due to the need for the simpler and more accurate methods for the determination of ions of the alkali metals. Special attention has been given to the determination of sodium and potassium because of their importance in biological systems. Although flame spectroscopy was first studied by Bunsen and Kirchoff, it was Lundengarh who studied flame photometry exhaustively and established it as the most important analytical method for the estimation of alkalies.

In this methods of analysis, a test solution is atomized and blown into the gas burner and the intensity of colour lines of the spectrum isolated by filters is measured by a photocell. This is a measure of concentration of the element.

### 4.2 Principle

Trace amounts of sodium and potassium can be determined by flame emission photometry at a wavelength of 589 and 766.5 nm respectively. The sample is sprayed into a gas flame and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters or by a suitable slit arrangement in light-dispersing devices such as prisms or gratings. The

intensity of light is measured by a phototube potentiometer or other appropriate circuit.

#### 4.3 Interference

Flame photometers operating on the internal standard principle may require adding a standard lithium solution to each working standard and sample. The optimum concentration may vary among individual instruments.

Interference may occur at sodium to potassium ratios of 5:1 or greater. Calcium may interfere if the calcium to potassium ratio is 10:1 or more. Magnesium begins to interfere when the magnesium to potassium ratio exceeds 100:1.

#### 4.4 Instrument Description

The basic instrument consists of the following parts:

**Pressure regulators :** In order to achieve a steady state emission, it is of primary importance to have a flame that is perfectly steady. To ensure this, it is imperative that the air (or oxygen) and fuel pressure be maintained constant while flame photometer is in use.

**Atomiser :** Here the sample in the form of solution droplets is broken into fine particles and with the force of the compressed air or oxygen is carried to the flame.

**Optical system :** The function of the optical system is to collect the light from the steadiest part of the flame, render it monochromatic, and then focus it onto the surface of the photosensitive detector.

**Detector :** Most flame photometer employ phototubes and amplifier units to boost the output signals. In this respect, the

electron multiplier phototube provides the maximum signals and permits applying flame photometry to systems that are weak in emission either because of a small concentration of test element or because of difficulty in exciting any appreciable fraction of the test element under the excitation condition existing in the flame.

#### 4.5 Procedure

Follow manufacturer's recommendations for selecting proper photocell and wavelength, adjusting slit width and sensitivity, appropriate fuel and air or oxygen pressure, and the steps for warm up, correcting for interferences and flame background, rinsing of burner, igniting sample, and measuring emission intensity.

Start the electrical supply and switch on the air supply. Stabilize the air. This needle should be steady at the mark. Switch on the gas and maintain the gas fuel mixture so that the blue flame is seen through the viewing window.

Prepare a blank and sodium or potassium standards in stepped amounts in any of the following applicable ranges: 0 to 1.0, 0 to 10 or 0 to 100 mg/L.

Starting with the highest calibrating standard and working toward the most dilute, measure emission at the respective wavelength.

Prepare a calibration curve from the standards and determine concentration of sample from the calibration curve.

## 5.0 ION SELECTIVE ELECTRODE

### 5.1 General

An ion-selective electrode can be defined as an electrochemical sensor which responds to a specific ion in accordance with the Nernst equation.

$$E_{ISE} = E_0 + \frac{RT}{n} \ln a_x$$

Where:

$E_{ISE}$  = the electrode potential

$E_0$  = the standard potential of the electrode

$a_x$  = the activity of the ion x

n = the charge of the ion x

T = absolute temperature in °K

f = the faraday constant

R = the gas constant

The electrode potential of a sensor can not be measured directly but has to be determined on the basis of a complete electrochemical measuring chain consisting of the ion-selective electrode and a reference electrode. The measured potential  $E_{chain}$  will then be given by the espression :

$$E_{chain} = E_{ISE} + E_{ref} + E_j$$

Where:

$E_{ISE}$  = the potential of ion-selective electrode

$E_{ref}$  = the potential of reference electrode.

$E_j$  = the liquid junction potential between the reference electrolyte and the sample.

$E_{ref}$  and  $E_j$  are normally constant.

Ion-selective electrode can be classified according to the type of active material used for the membrane. The main classes of sensors may be identified as follows:

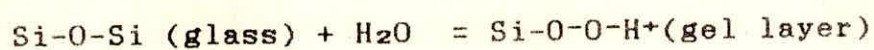
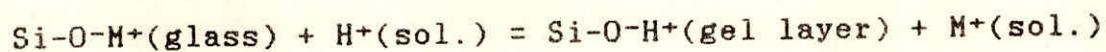
- Glass electrodes
- Solid-state electrodes
- Organic ion-exchanger electrodes.

Glass electrodes may also be classified as solid-state electrodes, but are normally considered as a special class (Figure 2). Practical applicable glass electrodes are the hydrogen ion electrode and the sodium electrode. The ion to which the electrode responds depends on the composition of the glass membrane.

The hydrogen electrode is the best behaved ion-selective electrode with rather unique properties compared with other types of ion-selective electrodes. The dynamic range of this electrode is almost 14 decades of concentration, the response time is very short and the selectivity extremely high.

A glass electrode only functions satisfactorily when the glass membrane has a hydrated layer on its surface. A swollen hydrated layer is formed spontaneously on the surface when the glass electrode is left in an aqueous solution. The thickness of the hydrated layer is approximately  $10^{-6}$  cm. At the interface of the hydrated layer with a sample, the sodium or lithium ions in the glass are exchanged with hydrogen ions in the sample. (The surface acts as a cation exchanger).

The formation of the gel-layer takes place in accordance with the following reactions:

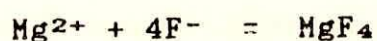
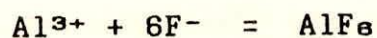


M<sup>+</sup> is a monovalent cation, e.g., Na<sup>+</sup> or Li<sup>+</sup>.

The sodium glass electrode is a further development of the hydrogen ion electrode, where the alkaline error has been increased. This is obtained by introducing Al<sub>2</sub>O<sub>3</sub> into the glass. The sodium electrode will still be more sensitive for hydrogen ions than sodium ions, but this can be overcome by making the samples alkaline.

Solid state electrodes have an ionically conducting membrane, which is based upon one or more inorganic salts. The membrane can be a single monocrystal (e.g., LaF<sub>3</sub>), polycrystalline (As<sub>2</sub>S) or a mixed membrane with silver sulfide as the main substance (Figure 3&4). The solubility of the inorganic salt used for the membrane has to be very low, as the detection limit for the electrode depends upon the contribution of ions from the membrane to the sample.

The most popular solid-state electrode is without doubt the fluoride electrode, the membrane of which consists of lanthanumtrifluoride. The fluoride ion transports the charge on the membrane. The hydroxide ion causes interference, and Al<sup>3+</sup> and Mg<sup>2+</sup> builds complex compounds with F<sup>-</sup>.



To relax the fluoride ion from these complex compounds before measurement, a so-called TISAB-solution (Total Ionic Strength Adjustment Buffer) has to be added to the sample before measurements.

Chloride, bromide and iodide selective electrodes are based upon silver halogenide crystals, where the silver ion transports the charge. The detection limit is determined by the solubility of the silverhalogenide. Also the sulfide electrode utilizes the silver ion as a charge carrier, as its membrane is polycrystalline  $\text{Ag}_2\text{S}$ . The cyanide electrode is based upon a membrane of silveriodide. When measuring with the cyanide electrode, the silver iodide will be dissolved as the iodide ions are exchanged with cyanide ions.



$\text{Ag}(\text{CN})_2$  is a soluble complex, and this is the reason why the life time of the cyanide electrode is reduced by frequent measurements in solutions with high cyanide content.

For continuous use of the cyanide electrode, it is therefore advisable to ensure that the concentration does not regularly exceed  $10^{-3} \text{ M CN}^-$ .

The copper electrode is another solid-state electrode. The membrane composition can be  $\text{CuS}$  or  $\text{CuS/Ag}_2\text{S}$ .

A special type of solid-state electrode is the so-called Ruzicka Electrode (Figure 5), which is a multipurpose electrode. The properties of the electrode can be changed by replacing the electroactive layer. The electrode consists of a teflon stemtube, into which a teflon graphite body is fitted. An

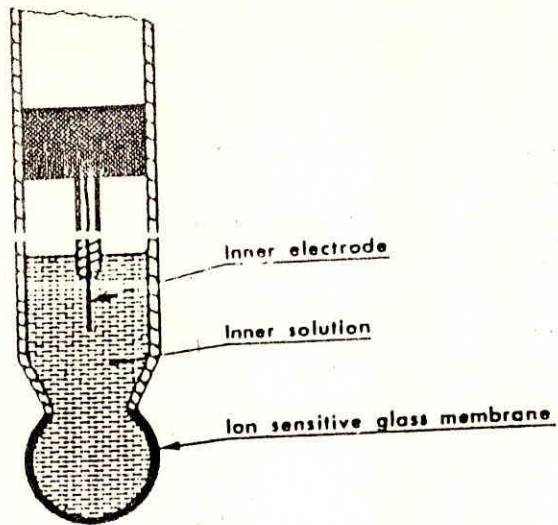


FIGURE 2: GLASS ELECTRODE

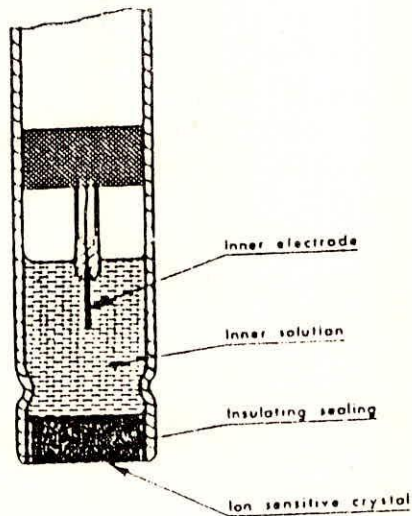


FIGURE 3: SINGLE CRYSTAL MEMBRANE ELECTRODE



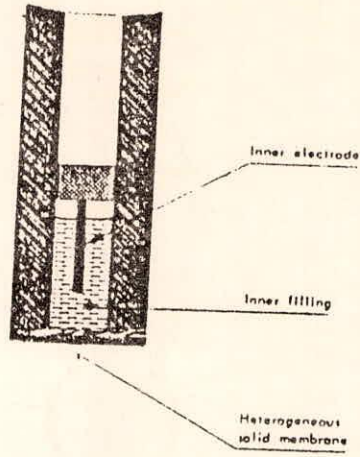


FIGURE 4: HETEROGENEOUS MEMBRANE ELECTRODE

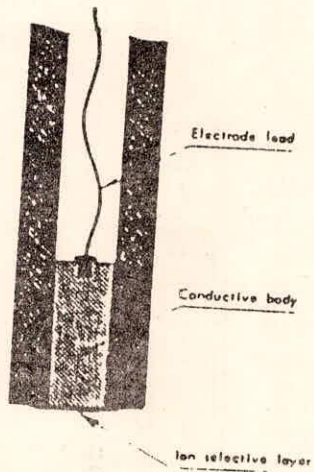


FIGURE 5: RUZICKA ELECTRODE

electroactive powder sensitive to the particular ion to be measured is rubbed into the teflon-graphite surface before measurements are made. The powder is easily replaced with another electroactive powder sensitive to a different ion, if desired. The ion-sensitive powder is based upon silver sulfide as the main substance, into which either a silverhalogenide or a heavy metal sulfide is mixed, depending upon the purpose. In this way the same electrode may be impregnated with powders for the determination of  $\text{Ag}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$  or the redox potential.

The third class of ion-selective electrodes is the ion-exchanger electrodes, where an ion-exchanger is the active component in the membrane. The class comprises the potassium, the calcium and the nitrate electrodes.

In the potassium electrode the ion-exchanger is valinomycin which is an antibiotic (valinimycin is a neutral carrier). The valinomycin has a closely knit structure with a central cavity. The potassium ion is similar in size to the cavity and therefore tailored to form complexes with the valinomycin molecule. Due to this tailored fitting, the selectivity properties of the potassium electrode is rather unique. The interference from other monovalent ions is very low, and the electrode is 10 times more sensitive to  $\text{K}^+$  than to  $\text{Na}^+$ . The valinomycin is normally incorporated in an inert matrix such as PVC.

The calcium electrode is based upon organic calcium phosphate compounds (e.g., calcium di-(n-octylphenyl) phosphate)

as ion exchanger. The ion exchanger is incorporated in PVC-membrane and dioctyladepate is used as plasticizer.

The nitrate electrode is based upon organic ammonium nitrate compounds incorporated into a PVC-membrane.

An important thing to note about ion exchanger electrodes is, that the ion exchangers slowly dissolve in water, and this affects the membrane lifetime. The membrane must therefore be replaced after some time. Manufacturers of this class of electrodes normally deliver extra membrane material with each electrode, so that the customer can renew the membrane, when required.

## 5.2 Principle

The basic equation for measurements with ion-selective electrodes is the Nernst equation, which gives the relationship between the electrode potential and the activity of the specific ion.

$$E = E_0 + RT/nF \ln a_x = E_0 + 0.198 T/n \log a_x$$

where

$E$  = the electrode potential in mv

$E_0$  = the standard electrode potential

$T$  = the absolute temperature in °K

$F$  = the Faraday constant (96489 coulombs)

$R$  = the gas constant

$n$  = the charge of the ion  $x$

$a_x$  = the activity of the ion  $x$

the factor  $0.198 T/n$  is called the Nernst factor, and has the value 59 mV at 25°C for a monovalent ion.

### 5.3 Interference

Every electrode is susceptible to some interferences depending on the selectivity coefficient of the electrode.

### 5.4 Instrument Description

Every electrode assembly consists of an indicating electrode selective to a particular ion and a reference electrode. The indicating electrode changes its potential in response to the activity of the measured ion, where the reference electrode provides a constant reference potential. The most common reference electrodes are the calomel and the silver/silver chloride type. They consist of a half-cell, which is immersed in an electrolyte solution in contact with the sample by diffusion. The diffusion takes place through a porous pin or glass sleeve connection, known as liquid junction.

### 5.5 Procedure

Ion-selective electrodes offer several approaches to measuring practice. Ion-selective electrodes sense the activity of the ion in solution, but by various measurement techniques it is possible also to determine the concentration of the ions.

The most important techniques are direct potentiometry, standard addition/subtraction methods and titrations. With concentration measurement by direct potentiometry at least two standard solutions have to be used. One solution with a higher concentration than the sample and one with a lower. Often a dilution series of standard solutions may be used.

It is important that the sample and the standard solution are as equal in composition as possible, so that matrix

effects are avoided. Therefore the ionic strengths of the standard solutions have to be adjusted so that they correspond to the ionic strength of the sample.

The ionic strength can be adjusted by addition of a highly concentrated electrolyte to both sample and standard solutions. If necessary a buffer solution and decomplexing agent can also be added, e.g., when analyzing drinking water for fluoride ions, a so-called TISAB-solution (Total Ionic Strength Adjustment Buffer) is added to the water and standards before measurements. Further, it is important that the temperature of the standard solutions and the sample is same.

## 6.0 TOTAL ORGANIC CARBON ANALYSER

### 6.1 General

Measurement of total organic carbon (TOC) is a much more rapid means of determining the organic content of water and wastewater than is the measurement of biochemical oxygen demand (BOD) or chemical oxygen demand (COD). BOD is not directly related to total organic content due to the presence of non biodegradable organic compounds and COD analysis may include reduced inorganic compounds. However, if the relative concentrations of organic compounds in the samples do not change greatly, empirical relationships can be established between TOC and BOD or COD to permit convenient estimation of latter.

### 6.2 Principle

The organic carbon present in the sample is oxidized to carbon dioxide by persulfate in the presence of ultraviolet light. The carbon dioxide produced is measured directly by a non-dispersive infrared analyser. The homogeneous samples when injected in the total carbon channel or inorganic carbon channel respectively, converts the carbon present in samples into carbon dioxide. The percentage of carbon present in samples are given in terms of percentage of carbon dioxide which is measured by non-dispersive infrared analyser. The difference of readings between total carbon and inorganic carbon gives organic carbon present in the sample.

### 6.3 Interference

Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile

organic substances. Another important loss can occur if large carbon containing particles fail to enter the needle used for injection.

#### 6.4 Instrument Description

The basic instrument consists of the following:

Flow system : Two channels have different pressure regulators, pressure guage, flow control valves and flow meters for carrier gas. The gas then flows through reaction chamber and then condenser to remove steam and then in turn to infrared analyser and in atmosphere.

Combustion tube : In the total carbon channel a high temperature furnace heats a ceramic combustion tube containing cobalt oxide deposited on an inert substrate. The temperature of furnace is maintained at 950°C. The oxygen in the carrier gas oxidises both organic and inorganic carbonaceous material to CO<sub>2</sub> and steam.

In the inorganic carbon channel a low temperature furnace heats a glass tube containing quartz chips wetted with 85 % phosphoric acid. The temperature of furnace is sufficiently high for the desired reaction but substantially below that required to oxidise organic matter. The acid liberates CO<sub>2</sub> and steam from inorganic carbonates.

Electrical System : The power to both the furnaces are supplied through adjustable temperature controller assembly utilising thermocouple as sensor. The Thermocouple and associated SCR and resistances constitute a bridge. Deviation of furnace temperature from the selected set point unbalances the bridge and

causes the required increase or decrease in heater voltages.

Electronic Circuitary for Infrared Analyser : The Infra-red energy is produced by two separate energy sources. then it is passed through optical filters to minimise interference and to the cells where one has non-absorbing gas and other a continuous flowing samples and finally on detector.

Chart Drive Recorder: Out put from infrared analyser is fed to the recorder which is sufficient to drive the pen motor for full span. The adjustment for the chart speed and full scale span is done according to requirement.

#### 6.5 Procedure

A water sample is introduced into the instrument either by syringe injection or by means of a calibrated sample loop followed by known amount of acid into the digestion vessel. The sample loop affords greater consistency of injection volume, whereas the syringe injection pot allows injection of microliter quantities of samples of extremely high carbon concentration.

After acid been added, a gas stream purges out any carbon dioxide formed from inorganic carbon in the sample. This carbon dioxide is carried to a molecular sieve trap held at 25°C where it is trapped and concentrated.

When purging and trapping is complete, the trap is placed in line with the infrared detector and rapidly heated to 200°C. A stream of gas desorbs the carbon dioxide from the trap and carries it into the detector. The detector response represents the amount of total inorganic carbon (TIC) in the sample.



While the carbon dioxide from TIC is being detected, a known amount of sodium persulfate is added to the sample, which by now has been heated to 100°C. meanwhile, purge gas flow to the digestion vessel has been shut off. The persulfate reacts with organic carbon in the sample to produce carbon dioxide, which accumulates in the digestion vessel.

After a preset reaction time, the digestion vessel is replaced in-line with the trap and a gas stream purges out any carbon dioxide produced by the persulfate oxidation.

This carbon dioxide is carried to the trap held at 25°C where it is trapped and concentrated.

The trap is then again placed in-line with the detector and heated. The carbon dioxide is carried into the detector, and the resulting concentration of TOC in the sample is displayed.

While the carbon dioxide from TOC is being detected, gas flow in the digestion chamber is reversed, and the spent sample is carried out of chamber to drain.

The purge gas flow is returned and a known amount of acid is added to rinse the bottom of the digestion vessel. The system is then drained again and is ready for new sample.

Total carbon is determined by the measurement of carbon dioxide released by the complete oxidation of all carbon present in the sample (inorganic and organic). For this analysis, acid and persulfate are added together with the sample at the beginning of the analysis and allowed to react for a specified time converting all carbon present to dissolved carbon dioxide. When the reaction is complete, the resultant carbon dioxide is purged

from the solution, concentrated by trapping and detected as described for TIC above

## 7.0 ATOMIC ABSORPTION SPECTROPHOTOMETER

### 7.1 General

Atomic absorption spectrometry (AAS) enables metallic elements to be determined with remarkable sensitivity and accuracy and is currently the most prevalent method of metal analysis in water and effluents. Almost every known metallic element can be determined by using this technique. In most cases, trace amount of an element can be determined in the presence of much higher concentration of other elements.

Two important reasons for the widespread use of atomic absorption spectrophotometric analysis are i) sample preparation, in most instances, can be kept to a minimum for a great number of elements, and ii) ease of instrument operation and sensitivity compete with most analytical methodology.

### 7.2 Principle

Atomic absorption measurement is based on the amount of light which is absorbed by an atomic vapour as the light passes through a cloud of atoms. If energy of the right magnitude is applied to an atom, the energy will be absorbed by the atom, and an outer electron will be promoted to a less stable configuration or excited state. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others.

### 7.3 Interference

The most troublesome type of interference result from the lack of absorption by atoms bound in molecular combination in the flame. This can occur when the flame is hot enough to dissociate the molecules or when the dissociated atom is oxidized immediately to a compound that will not dissociate further at the flame temperature. Such interferences may be reduced or eliminated by adding specific elements or compounds to the sample solution. For example, the interference of phosphate in the magnesium determination can be overcome by adding lanthanum. Similarly, introduction of calcium eliminates silica interference in determination of manganese.

### 7.4 Instrument Description

The basic instrument consists of the following parts as shown in figure 6.

**Light Source :** The two most common light sources used in atomic absorption are the hollow cathode lamp and the electrodeless discharge lamp. The hollow cathode lamp is an excellent, bright line source for most of the elements determinable by atomic absorption. The cathode of the lamp is a hollowed-out cylinder of the metal whose spectrum is to be produced. The anode and cathode are sealed in a glass cylinder filled with either neon or argon gas at low pressure. A window transparent to the emitted radiation is fused to the end of the cylinder. When electrical potential is applied between cathode and anode, a bright discharge appears at the cathode emitting a narrow beam of characteristic line of element. Separate hollow

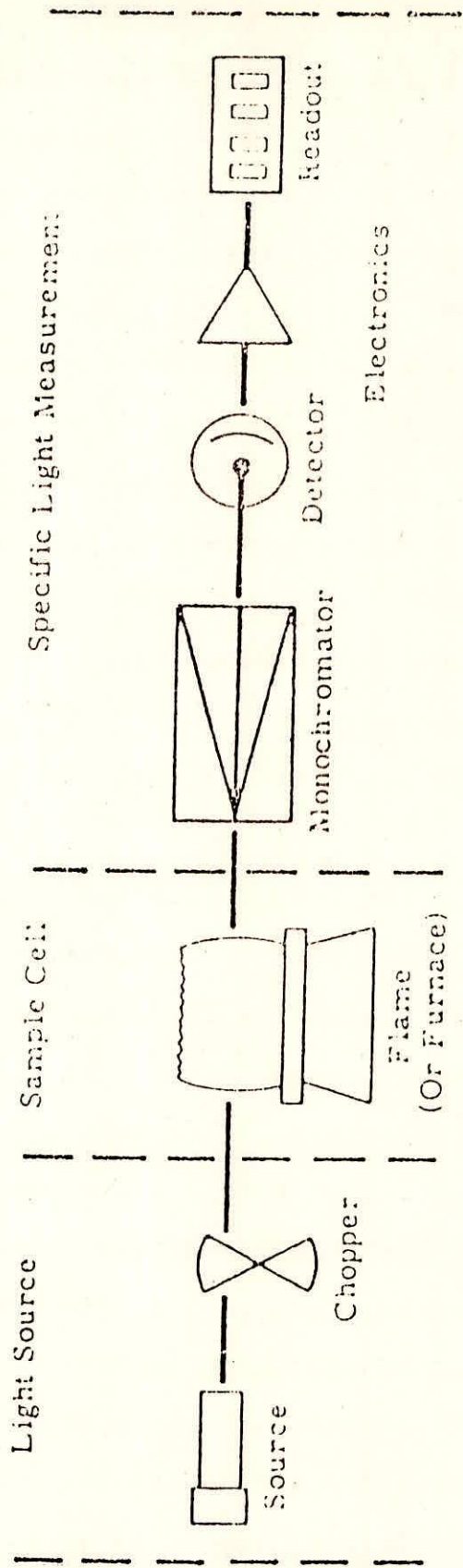


FIGURE 6: LAYOUT OF ATOMIC ABSORPTION SPECTROPHOTOMETER

cathode lamp has to be used for every element to be determined.

**Atomizer** : The most routine and widely applied sample atomizer is the flame. Only a small portion of the sample is introduced into the burner chamber by the nebulizer. The finest droplets of sample mist or aerosol are carried with the combustion gases to the burner head, where atomization takes place.

**Buner and Flame** : A premix type, long path length laminar flow slot burner is normally used. Commonly used flames are air-acetylene and nitrous oxide-acetylene.

**Monochromator** : A diffraction grating type monochromator is used. Light from the source enters the monochromator at the entrance slit and is directed to the grating where despression takes place. The diverging wavelengths of light are directed towards the exit slit. By adjusting the angle of grating, a selected emission line from the source can be allowed to pass through the exit slit and fall onto the detector. All other lines are blocked from exiting.

**Detector** : Most widely used detector for AAS is the photomultiplier tube (PMT). It is a vacuum tube that contains a photosensitive material called photocathode, that eject electrons when it is struck by light. These ejected electrons are accelerated towards a dynode which ejects two to five secondary electrons for every one electron which strikes its surface. The secondary electrons strike another dynode, ejecting more electrons which strike yet another dynode, causing a multiplicative effect along the way. Typical PMT contains 9 to 16

dynode stages. The final step is the collection of the secondary electrons from the last dynode by the anode. The electrical current measured at the anode is then used as a relative measure of the intensity of the radiation reaching the PMT.

Amplifier and Read-out : Signal from the photomultiplier is amplified several times and is fed to a absorbance meter. The amplifier is tuned to the same frequency of modulation of the hollow cathode lamp which is also modulated to cut off the background noise.

Electronics : Most modern atomic absorption instruments include microcomputer based electronics. The microcomputer provides atomic absorption instruments with advanced calculation capabilities, including the ability to calibrate and compute concentrations from absorption data conveniently and accurately, even for non-linear calibration curves.

#### 7.5 Procedure

Install a hollow cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to table 1. Set slit width according to manufacturer's suggested setting for element being measured. Turn on instrument, apply to the hollow-cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally 10 to 20 min. Readjust current as necessary after warm up. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified and ignite flame. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Atomize a standard (usually one near the middle of the linear working range) and adjust burner both up and down and sideways to obtain maximum response. Record absorbance of this standard when freshly prepared and with a new hollow-cathode lamp. The instrument now is ready to operate.

Select at least three concentrations of each standard metal solution to bracket the expected metal concentration of a sample. Aspirate each in turn into flame and record absorbance. For Cr calibration mix 1 mL 30%  $H_2O_2$  with each 100 mL Cr solution before aspirating. For Fe and Mn calibration, mix 100 mL of standard with 25 mL Ca solution before aspirating.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step may be avoided. Plot calibration curves based on original concentration of standards before dilution with lanthanum, calcium or hydrogen peroxide solution.

Rinse nebulizer by aspirating water containing 1.5 mL concentrated  $HNO_3/L$ . Atomize blank and zero instrument. Atomize sample and determine its absorbance.



When determining Ca or Mg, dilute and mix 100 mL sample with 10 mL lanthanum solution before atomization. When determining Cr, mix 1 mL H<sub>2</sub>O<sub>2</sub> with each 100 mL sample before aspirating.

Determine concentration of each metal ion from the appropriate calibration curve.

Table 1. Atomic Absorption Concentration Ranges with Direct Aspiration Atomic Absorption

Element	Wave length mm	Flame Gases	Detection Limit, mg/L	Sensitivity mg/L	Optimum Conc range, mg/L
Cd	222.8	A-Ac	0.002	0.025	0.05-2
Ca	422.7	A-Ac	0.003	0.08	0.2-20
Cr	357.9	A-Ac	0.02	0.1	0.2-10
Co	240.7	A-Ac	0.03	0.2	0.5-10
Cu	324.7	A-Ac	0.01	0.1	0.2-10
Fe	248.3	A-Ac	0.02	0.12	0.3-10
Hg	253.6	A-Ac	0.2	7.5	10-300
Pb	283.3	A-Ac	0.05	0.5	1-20
Mg	285.3	A-Ac	0.0005	0.007	0.02-2
Mn	279.5	A-Ac	0.01	0.05	0.1
Ni	232.0	A-Ac	0.02	0.15	0.3-10
K	766.5	A-Ac	0.005	0.04	0.1-2
Ag	328.1	A-Ac	0.01	0.06	0.1-4
Na	589.0	A-Ac	0.002	0.015	0.03-1
Sr	460.7	A-Ac	0.03	0.15	0.3-5
Zn	213.9	A-Ac	0.005	0.02	0.05-2

A-Ac = Air-Acetylene

## 8.0 CONCLUSION

Micro and macro estimation of various water quality parameters are essential in water quality management. Instrumentation and instrumental techniques play a vital role in monitoring water quality of various water bodies. Various techniques included in this report are flame photometry, ion selective electrodes, total organic carbon analyser and atomic absorption spectrometry. Emphasis has also been given on conventional instruments like pH meter, turbidity meter, etc., with a view to increase their performance and reproducibility. This report, describing various aspects of instrumental analysis, should prove useful for scientists and technologists engaged in water quality monitoring.

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