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PHYSICO CHEMICAL ANALYSIS OF WATER AND WASTEWATER

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ABSTRACT

Water and waste water analysis have become increasingly important in water quality monitoring. Analytical techniques adopted for monitoring should be precise and accurate. The method should take into consideration the limitations in the developing country situations. Analytical procedures for measurement of various water quality parameters have been developed and are readily available in manuals of standard procedures. Standard methods for the examination of water and wastewater,published jointly by the American Public Health Association, the American Water Works Association and the Water Pollution Control Federation, is well knownin the field of water analysis.

The present manual is an attempt to collate and synthesize much of this information in a simplified form in order to serve as an aid to practical work. The analytical methods recommended in this report have been selected on the basis of their wide applicability and their general acceptability. The details of each test procedure is described as general principle, chemicals required for tests, the method of calculations and its significance.

Under 'sampling' a brief statement describes sampling precautions that may be required and specifies the type of container to be used. Information is also given on any preliminary treatment required. The manual also describes specific steps which must be taken both at the time of sampl-ng and during storage to maintain the integrity of the

sample.

Under 'analysis' detailed procedure and method of calculations have been given. For all the methods, the form and units of reporting values for physical and chemical quality parameters and constituents are specified. The proper number of significant figures to be used in reporting analytical measurements are specified to indicate the confidence level that the data may expect.

1.0 INTRODUCTION

1.1 General

The term water quality is a widely used expression which has an extremely broad spectrum of meanings. Each individual has vested interests in water for his particular use, which may involve commercial and industrial uses. Since the desirable characteristics of a water vary with its intended use, there is frequently unsatisfactory communication among the users of water where quality is concerned.

From the standpoint of water quality there are many variations. There are waters with extremely low concentration of a few ions and others which have high concentrations of ions of many different kinds. there are of-course transitions between the extremes.

Even today man has brought about changes, whether through urbanisation and growth of population centres, or by introduction of industries and employment of auxiliary means in agriculture, which has disturbed or even destroyed the natural, healthy quality of water bodies in many regions. These water bodies have become unsuitable for many beneficial uses. Furthermore, there is a world wide increase in the demand for good quality water. It has become imperative of protect and conserve the waters of the world not only as a resource for their present uses but also for their prospective uses. Water bodies also have to be considered as an essential component of a healthy landscape. Their protect is not only extremely urgent in the area which are heavily polluted but is also necessary as a precautionary measure for the conservation of undamaged areas.

A water quality management programme requires information including the existing water quality, the influence of man's activities on water quality, and criteria for the present and planned uses. In many instances, this information can be generated only from a record of long term water quality data and past experience of use of water of known quality for various purposes. Further, in order to enforce the laws developed on the basis of the above information and to evaluate the effectiveness of the programme,it has become more important to appraise water quality on a continuous basis. There are three basic criteria to evaluate the quality of water viz. the physical, chemical and biological.

The physical and chemical methods are concerned with a variety of procedures, each applicable to a particular situation. In many instances a combination of chemical analysis is needed to obtain a resonably accurate picture of the quality of water. Many of the chemical methods serve as an indices of past pollution of organic origin. The customary methods for biological analysis refer to pollution evaluation in terms of the presence and relative abundance of interstinal bacteria and other microscopic organisms.

The purpose of the analysis is to know the exact composition of the sample at the particular point of time of sample collection. After analysis is over, the results may be interpreted to suit a particular purpose of either surveillance of water quality,of effluent quality or to assess the performance of waste water treatment plant.

This manual is an attempt to collate and synthesize much of this information in order to serve as an aid to practical work. The analytical methods described here in have been selected on the basis of their wide applicability and their general acceptability. In the selection of methods, full use was made of authoritative, widely used references. Standard Methods for the Examination of Water and Waste Water, is well known in the field of water anlaysis. Another is the Book of ASTM Standards, part 31, revised and published annually by the American Society for Testing and Materials. Two publications by Federal agencies were used in the selection of methods. One of these is methods for 'Collection and Analysis of Water Samples for Dissolved Minerals and Gases'. The other is a publication of the Environmental Protection Agency 'Methods for Chemical Analysis of Water and wastes'.

1.2 Parameters

The choice of parameters to be tested is closely linked to the objective of the water-quality survey programme and to available manpower and financial resources. Table 1 lists the major ions and physical parameters which will provide considerable information on the quality of water being evaluated. Test results on these parameters may be used for interpretive studies with respect to the Chemical quality of Water for domestica and industrial water supplies and other uses.

TABLE 1: PHYSICAL CHARACTERISTICS AND SOME MAJOR IONS AND INSTRUMENTATION

Parameter	Method	Instrumentation/apparatus
PHYSICAL CHARACTERISTICS:		
Colour	Colorimetric	Spectrophotometer
Conductivity	Electrical	Conductivity Meter
Turbidity	Turbidimetric	Turbidimeter
Residue	Gravimetric	Volumetric glassware
MAJOR CATIONS:		
Calcium	Titration	Volumetric glassware
Magnesium	Titration	Volumetric glassware
Sodium	Flame emission	Flame Photometer
Potassium	Flame emission	Flame Photometer
MAJOR ANIONS:		
Carbonate	Titration	Volumetric glassware
Bicarbonate	Titration	Volumetric glassware
Sulphate	Turbidimetric	Turbidimeter
Chloride	Titration	Volumetric glassware
OTHERS:		
Nitrate	Colour development with absorption measurement	UV-VIS Spectrophotometer
Silica	Colour development with absorption measurement	UV-VIS Spectrophotometer

The major ion results may be grouped into the anionic and cationic constituents. The accuracy of the analyses may be determined by comparing the sum of anions in equivalents per million (eqm) with the sum of the cations in epm (ionic balance). The percent error may be calculated as follows:

$$\text{Percent error} = \frac{\text{Sum of cations (epm)} - \text{Sum of anions(epm)} \times 100}{\text{Total ions(epm)}}$$

Analytical results in mg/L are converted to epm by dividing the actual concentration of the ion in mg/L by the equivalent weight of the ion. Theoretically the sum of the cations in epm should be equal to the sum of the anions in epm but these may differ by certain percentage points depending upon the accuracy of the analytical method used and the quality of the water being tested. Percent error of upto 1% are usually considered excellent while the higher percent error should alert the analyst to check his analysis or to determine the cause for such error.

In ionic balance determinations, calcium, magnesium, sodium and potassium ions form the cationic group while bicarbonate, sulfate and chloride ions form the anionic group. Other ions are usualy present in such low concentrations that they are not considered in the ionic balance. In cases where appreciable quantities of ion are present, soluble iron (Fe^{++}) will be included in the cationic group. Similarly, when carbonates and nitrates are present in significant amounts, these are included in the anionic group.

Table 2 tabulates other analytical measurements

TABLE 2 : SOME NUTRIENTS AND ORGANIC PARAMETERS

Parameter	Method	Instrumentation/appratus
NUTRIENTS:		
Phosphate	Colour development with absorption measurement	UV-VIS spectrophotometer
Inorganic Nitrogen (Nitrate,Nitrite etc.)	Colour development with absorption measurement	UV-VIS spectrophotometer
Total Kjeldahl Nitrogen(TKN)	Digestion and titration	Total Kjeldahl Nitrogen digestion apparatus
Silica	Colour development with obsorption measurement	UV-VIS spectrophotometer
WASTES:		
Dissolved Oxygen (DO)	Fixation and titration	Volumetric glassware
Biochemical Oxygen Demand (BOD)	Incubation and titration	Incubator and volumetric glassware
Chemical Oxygen Demand(COD)	Refluxing and titration	Volumetric glassware
Total Organic Carbon (TOC)	Ignition	Total Organic Carbon Analyser

which indicate nutrient concentrations in water,thereby providing information on the potential for vegetational growth and oxygen depletion in the water source. These measurments provide essential information on nutrient loadings from industrial, municipal and other sources to rivers, lakes and occans. Silica and nitrate are included in table 1 under major ions but they also appear in table 2 because they are considered as significant nutrients in water

An analytical capability to detect and measure metals and trace elements is most important particularly for monitoring the effects of mining and industrial activities on the aquatic environment. Two broad approaches to the determination of metals and trace elements should be taken when evaluating the economics of methodologies. The first includes the classical colourimetric method in which the absorption of coloured complex is measured on a spectrophotometer. These methods are generally time-consuming and do not always possess the sensitivity and selectivity desired. The other approach is atomic absorption spectrophotometer which are now readily available and are noted for their ease of operation, sensitivity, and applicability to a large number of elements in a wide variety of waters.

Table 3 lists metals most commonly measured in water. This list may be expanded to incorporate other important elements and substances as the need arises.

Another group of chemicals requiring identification and quantification is in the field of organic chemistry.

TABLE 3 : HEAVY METALS AND ELEMENTS

Parameter	Method	Instrumentation
Cadmium	Atomic absorption measurements	Atomic absorption spectrophotometer
Calcium		
Chromium		
Copper		
Iron		
Lead		
Magnesium		
Manganese		
Mercury		
Nickel		
Silver		
Strontium		
Zinc		

Pesticides, herbicides certain petroleum products, and many other organic materials are in this group. Table 4 tabulates some of the most common materials to be considered in this group. Two publications by Environmental Protection Agency may be consulted for the analysis of pesticides. One of these is Method for Organic Pesticides in Water and Waste-Water ' and other is 'Method for Organochlorine Pesticides in Industrial Effluents'.

Becteriological assessment of water should also be considered for water quality and water resources studies. Initial tests may include total coliforms, faecal coliforms, and faecal streptococci, but the requirements of the study will generally dictate the parameters to be measured in this class. However, this aspect has not been covered in this manual.

1.3 Standards

As a first step in the prevention and control of pollution it is necessary to prescribe certain standards for the purity of water into which effluents have been discharged so that such receiving water courses could be used for various purposes.

When setting water-quality standards, other factors such as technological feasibility should also be considered in addition to the possible effects on human health or aquatic organisms. Such standards should, of course, minimize all the known environmental and health hazards and should be regularly reviewed in the light of new knowledge. Since

TABLE 4 : PESTICIDES,HERBICIDES AND OTHER COMPOUNDS

Parameter	Method	Instrumentation
p,p' DDD	Injection into a gas chromatograph	Gas chromatograph with compressed gases.
p,p' DDT		
p,p' Methoxychlor		
Heptachlor		
Aldrin		
Chlordane		
Dieldrin		
Lindane		
2,4-D		
2,4,5-T		
Light and heavy petroleum products		

water quality should always be considered in relation to the intended use of water, there is no unique set of standards for streams, lakes or ground water, and the problem can not be solved in a general way.

The stream (or river) standards and the effluent standards are the two most common practices for the administration of water pollution. In the practice of stream standards, the waste water discharge is permitted to enter the river without violating the river water quality standards established by the appropriate authority. The discharger has the responsibility to maintain the river at its prefixed desired water quality level. It involves the established theoretical permissible values of the various pollutants relevant to the best use, existing pollution in the river, dilution available, self purifying ability of the river etc.

Water quality standards are usually issued on the national level based on the water-quality goals of the country. Indian standards prescribed by Bureau of Indian Standard have been compiled and given in Appendix-I.

1.4 Scope of the Manual

Agencies like water works, industrial organisations, water pollution Control Boards are required to analyse water and waste water samples. The present manual is an attempt to provide relevant information for testing of water and wastewater. The analytical methods recommended in this manual have been selected on the basis of their wide applicability and their general acceptability. Methods for use both in the laboratory and in the field are included. In the selection of methods, full use have been made of authoritative, widely used references. The details of each test procedure is described as general principle, interferences involved, chemicals required for tests,the method of calculations and significance of parameter. Standards recommended by Bureau of Indian Standard are also given for ready reference.

2.0 SAMPLING

Sampling is the first of a series of steps leading to the generation of water-quality data and is an exceedingly important one. Care must always be taken to ensure obtaining a sample that is truly representative. Further, the integrity of the sample must be maintained from the time of collection to the time of analysis. If the sample is not representative of the system sampled or if the sample has changed in chemical composition between sampling and analysis, all care taken to provide an accurate analysis will be lost.

2.1 Representative Samples

Chemical elements and compounds are distributed throughout the hydrologic environment - the atmosphere, precipitation, surface water, ground water, suspended sediment, bottom deposits, flora and fauna. Measurement in each component are important and validity begins immediately upon sampling. Irrespective of scrutiny and quality control applied in performing laboratory analysis, reported data are no better than the confidence that can be placed in the representativeness of the sampling.

In the case of dissolved constituents, dispersion is dependent on the vertical and lateral mixing within any given cross section of a body of water. The hydrologist collecting the samples must, therefore, not only be familiar with the mixing characteristics of streams and lakes, but must also have a good understanding of the role of fluvial-sediment transport and deposition.

2.2 Site Selection

Many factors are involved in the proper selection of sampling sites, including the following: objectives of the study, accessibility,flow mixing and other physical characteristics of the water body, chemical source locations, and personnel and facilities available to conduct the study.

Different agencies may have different objectives for assessing the water quality of streams, lakes and reservoirs. Most monitoring studies of streams and lakes are based on evaluating the effects of overland runoff, ground water inflow and/or waste disposal into water ways. Therefore, the study can usually be tied to the physiographic features of the area under consideration. In most cases, the quality of water flowing into a lake or past or particular point along a stream can be related directly to inputs within the drainage basin which includes the entire drainage area upstream of a selected point.

Whether the basic objective for the monitoring program be reconnaissance, long term trend evolution, or solving specific problems, the first step in the study is to define the appropriate hydrological boundaries and then to establish the sampling site locations above, within, or below these boundaries.

Accessibility to any sampling site is an obvious requirement and can be directly related to sampling costs. Bridges are normally the first choice for locating a stream sampling station since they not only provide ready access but also permit sampling at any point across the width of stream. Sampling locations on lakes and reservoirs, as well as those on larger rivers, may require the use of a boat. Frequently, however, the use of a boat will not only take more time in traversing a stream but also may prove difficult in the manipulation of the sampling equipment.

The ideal sampling station would be a cross section of a stream at which samples from all points on the cross section would yield the same concentrations of all constituents, and a sample taken at any time would yield the same concentration as one taken at any other time. This situation never persists in nature for any length of time, a fact which points to the need for careful site selection in order to ensure, as nearly as possible, uniform flow and good mixing conditions.

Availability of streamflow or sediment discharge records, or both, can be an important consideration in the selection of sampling sites on streams. Adequate discharge data are essential for estimating the total loads carried by the stream. If a gaging station is not conveniently located on a selected stream, the hydrologist should explore the possibility of obtaining discharge data by direct or indirect means.

The hydrologist must be aware of the locations of point and non point sources of chemical and physical constituents, such as industrial complexes, sewage outfalls, and agricultural wastes, so that he can select sampling sites which reflect the conditions set forth in the objectives. Representative measurement of a chemical constituent at a point on a main stream that is immediately below a source inflow or a tributary stream is usually impractical because frequently, the inflow closely follows the stream bank with little lateral mixing for some distance. One solution for avoiding this situation is to select a site above the chemical source or tributary stream, or to move the site far enough downstram to allow for adequate mixing and collection of representative samples.

2.3. Sampling Frequency

In conducing reconnaissance studies, both the bottom material and the overlying water should be sampled at each site. Monitoring which consists of repetative, continuing measurements to define variations and trends at a given location, should include collection of water samples at least monthly, with particular emphasis on extreme events. Bottom material samples should be collected from fresh deposition at least yearly at monitoring sites, and preferably during both spring and fall seasons.

2.4 Sample Collection

Sample collection in the water column varies in degree from the simplest of hand sampling procedures at a single point to the more sophisticated multipoint sampling techniques known as the equal discharge increment (EDI) method or the equal transit rate (ETR) method.

Generally, the number and type of samples to be taken depends on the width, depth, stream discharge, and the suspended sediment being transported. The larger the number of individual points sampled, the more nearly will the composite sample represent the water body.

Water is often sampled by filling a container held just beneath the surface of a body of water, commonly reffered to as a dip or grab samples. Published data reveal that a high percentage of samples are obtained in this manner. Using a weighed bottle holder which allows a sample bottle to be lowered to any desired depth, opened for filling, closed and returned to the surface, improves on this method. If an open bottle is lowered to the bottom and reaised to the surface at a uniform rate and at such a rate as to have the bottle just filled on reaching the surface, the resulting sample will roughly approach the collection of what is known as a depth integrated sample.

Many organic compound are only slightly water soluble they tend to be adsorbed by particulate matter in the water. This requires a sampling method that does not allow transfer of water from the sampling container without transfer of an appropriate amount of that suspended material.

Depth integration is used to collect a water sediment sample that weighted according to velocity at each increment of depth. This means that the water sediment mixture must enter the sample bottle at the same velocity as the flow passing the sample bottle intake. If the depth integrating sampler is lowered from the surface to the bed and back at the same rate, each increment of flow in that vertical is sampled proportionality to the velocity.

The open mouth weighted bottle sampler does not collect a truly representative sample in a flowing stream if there are many particles coarser than about 0.062 mm carried in suspension. Another, disadvantage in using an open mouth weighted bottle sampler in flowing streams is that there is no assurance as to when the bottle becomes filled. This compounds the uncertainty that the collected sample truly represents the distribution of both dissolved and suspended material in the sampled water column. Another sampling technique accepted by hydrologists for use in sand bed stream is the equal transit rate (ETR) method. With this method, depth integrating suspended sediment samplers are used to collect a velocity weighted sample. Samples are taken at a number of equally spaced verticals in the cross section depending on stream width. The transit rate of the sampler which is the rate of movement of the sampler from the surface to the bed and back to the surface, is the same at all verticals. The samples collected in each vertical are then composited into a single sample representative of the entire flow in the cross section. In this manner, the composite sample of the water sediment mixture flowing in the cross section is both velocity and discharge weighted.

It is recommended that all stream samples be collected by depth integrating methods using either a hand held or a cable and reel suspended sampler whenever it is practical to do so. the only exception might be in the case of shallow streams where the depth is insufficient to allow true depth integration. In such cases, dip samples collected at one or more verticals across the stream are appropriate, however, the sample container should be carefully held just beneath of water surface in order to avoid disturbing the stream bed.

The number of verticals to be sampled is usually decided by the person actually collecting the sample. For small streams, a depth integrated sample taken at a single transverse position located at the centroid of flow is adequate. Larger streams require sampling at several verticals at centroids of equal discharge increment (EDI). This method requires some knowledge of the stream flow distribution in the cross section before sampling verticals can be selected. To make an EDI measurement when prior streamflow data are not available, it is first necessary to determine the total discharge across the stream channel and then subdivide the cross section according to incremental discharges.

The number of verticals required for the equal transit-rate (ETR) method depends on the streamflow and sediment characteristics at the time of sampling as well as on the desired accuracy of the result. For all but very narrow and shallow streams, 10 to 20 verticals are usually sufficient.

The number of sampling sites on a lake or reservoir will vary with the size and shape of the basin. In shallow lakes having a circular basin, a single site in the deepest part of the lake may be sufficient to describe the distribution and abundance of the constituents in solution. In natural lakes the deepest point is often near the lake centre, and in reservoirs, the deepest area is near the dam. In lakes with irregular shape and with several arms and bays that are protected from the wind, additional sampling sites may be needed to adequately define the water quality.

Many lake measurements are now made in situ with the use of sensor probes and automatic readout or recording devices. Single and multiparameter instruments are available for measuring temperature, depth, pH,ORP, specific conductance, dissolved oxygen, some cations and anions, and light penetration.

Lake water samples may be collected at any disired depth with a Kemmerer-type sampler and brought to the surface for filtering or other pre-analysis treatment. Non-uniform vertical mixing of chemical constitutents often occurs because of wind and temperature changes, the shape of the lake basin, biological activity, and many other factors. Therefore, water samples should be collected from several points in the water column.

2.5 Sample Handling and Preservation

Thoroughly cleaned plastic or glass bottle fitted with screw caps may be used for water samples collected with depth integrating samplers. Plastic containers are generally preferred for inorganic samples and glass is preferred for organic samples. Plastic bottles must not be used for organic samples and certain trace metals because it is known that they introduce interferences and have sorption characteristics. A sufficient volume of sample should be collected to satisfy the requirements of each analysis and also to permit analysis of duplicate and fortified samples. Breakage of glass sample bottles can be overcome by shipping them in expanded polystyrene containers molded to fit the bottles.

Deteriorated samples negate all the efforts and cost expended in obtaining good samples. In general, the shorter the time that elapses betwen the collection of a sample and its analysis, the more reliable will be the analytical results. For certain constituents and physical values, immediate analysis in the field is required in order to obtain reliable results because the composition of the sample almost certainly will change before it arrives at the laboratory. However, some samples can be satisfactorily preserved by chilling or by adding suitable acid, or by other suitable treatment. They may then be allowed to stand for a longer period of time before analysis.

Determinations of temperature, pH, specific conductance, and dissolved gases should be made in the field. Samples for metal analysis can be preserved by addition of nitric acid, samples for organic constituent determination by chilling or freezing, and samples for the determination of such biodegradable substances as nitrates, phosphates and surfactants by chilling the sample immediately in an ice bath and storing the sample in the dark at a temperature just above freezing until the analysis are made. It is necessary however, to select the method of analysis and determine what preservative is recommended for that particular determination before adding a preservative to any sample because certain preservatives interfere with some determinations. A list containing methods of sample preservation and time allowed between sample collection and analysis is presented in table 5.

When it is required to determine concentration of dissolved inorganic constituents in a water system, the sample must be filtered through a 0.45 - μm average pore diameter membrane filter immediately after collection. It is advisable to discard the first 150 to 200 mL of filtrate in order to rinse the filter and filteration apparatus of any contaminating substances. This technique minimizes the risk of alteration of the composition of sample by the filtering operation. The filtrate, collected in a suitable bottle, usually polyethylene, is immediately acidified to pH 2.0 or less with nitric acid whose purity is consistent with the measurement to be made. Acidifying the filtrate (sample) minimize the risk of precipitation of dissolved constituents and also inhibits adsorption of constituents by the walls of the bottle. Samples treated in this manner may be used for the determination of dissolved constituents. Inorganic anionic constituents may be determined using a portion of the filtrate that has not been acidified.

When it is desirable to filter samples for analysis of organic constituents, a glass fiber or metal membrane filter should be used, and the sample collected in a suitable

TABLE 5 : SUGGESTED PRESERVATION TECHNIQUES

Parameter	Preservative	maximum storage time
Colour	Cool to 3-4°C	24 hrs.
Residue	Cool to 3-4°C	24 hrs.
Turbidity	Cool to 3-4°C	7 days.
pH	-	Immediately
Acidity	Cool to 3-4°C	24 hrs.
Alkalinity	Cool to 3-4°C	24 hrs.
Hardness	Add 2 mL HNO_3/L Cool to 3-4°C	7 days.
Sulfate	Cool to 3-4°C	7 days.
Chloride	-	7 days.
Fluoride	Cool to 3-4°C	7 days.
Dissolved oxygen	Collect in BOD bottle	Immediately
Phosphate	Cool to 3-4°C	24 hrs.
Nitrogen,ammonia	Add 2 mL H_2SO_4/L Cool to 3-4°C	7 days.
Nitrogen,nitrate	"	7 days.
Nitroge ,nitrate	"	7 days.
Silica	Cool to 3-4°C	7 days.
Biochemical oxygen Demand.	"	6 hrs.
Chemical Oxygen Demand.	Add 2 mL H_2SO_4/L	7 days
Total Organic carbon	Add 2 mL H_2SO_4/L	7 days
Oil & Grease	Add 2 mL H_2SO_4/L Cool to 3-4°C.	24 hrs.
Metals	Add 5 mL HNO_3/L	6 months

container,usually glass. In as much as most organic analysis require extraction of the entire sample, no portion should be discarded. After filtering, the membrane containing the suspended fraction may be scaled in a glass container and analysed separately.

The determinations of total recoverable inorganic constituents may be made on a second, unfiltered sample collected at the same time as the sample for dissolved constituents. It is advisable to acidify this sample also to avoid precipitation and adsorption. Portions of an unfiltered, acidified sample may be used to determine total or total recoverable metals, depending on the techniques used to bring the metals or other constituents into solution, or on the analytical techniques used for their determination.

A procedure sometimes used to determine suspended inorganic materials involves digestion of the material collected on the membrane filter in nitric or hydrochloric acid, or both. All or most of the particulate matter is thus brought into solution. The resulting digestate may be analysed by the usual means to determine either total suspended inorganic constituents or inorganic constituents recoverable by dilute acid digestion of the suspended matter. Such treatment of the suspended particulate matter obviously doubles the amount of analytical work required and consequently an analysis of an unfiltered acidified sample constitutes the morecommonly performed determination when information on more than just dissolved material is desired.

It should be noted that a true determination of the total concentrations of all inorganic constituents in a water suspended sediment mixture cannot be made unless the particulate matter is completely dissolved, or an analytical technique is used which does not discriminate between the chemical or physical forms of the constituents present in the sample.

3.0 ANALYTICAL PROCEDURES

3.1 Physical Parameters

3.1.1 Temperature

The temperature of water is one of the most important characteristics which determines, to a considerable extent, the trends and tendencies of changes in its quality. Temperature is an important factor affecting ion and phase equilibria, and influencing the rates of biochemical processes which accompany the changes of concentration and of content of organic and mineral substances. It is generally known that the rate of numerous chemical reaction including catalytic and enzymatic ones depends considerably on changes in temperature (on the average 2 to 3 times for every 10°C). Consequently, when discussing parameters such as sedimentation, mobilization of undissolved substances, solution of gases and their escape from water into the atmosphere, the processes of chemical and biochemical self-purification, formation of secondary pollutants, and others, it is necessary to know the temperature of the water, air and in some cases the bottom deposits.

Temperature data are also used when the degree of saturation of water by oxygen and other gases is calculated The shifting of various dynamic equilibria such as concentration of carbonates, sulphides, or degree of alkalinity, or electro conductivity, are also affected by temperature changes.

In some cases, temperature is the direct index of the influence of man-made factors on the quality of water (thermal pollution). The effect of thermal pollution on various physical, chemical and biological processes have been described by Jain and Bhatia (1986).

The temperature of the water and of the air is measured at the time when sample are taken, usually using mercury thermometers calibrated to a 0.1 to 0.5°C division. Thermometers contained in metal protective casings are available commercially for field work and are calibrated in scales suitable for normal water temperatures.

Water temperature may also be measured by electrical instruments equipped with thermistor-type sensors. these instruments may contain recording device for tabulating temperatures with time.

Oceanographic reversing thermometers are used to measure temperature in waters at various depths. The thermometer is lowered to the desired depth and turned over after five minutes. The temperature reading on the instrument is then fixed so that is does not alter as the thermometer is brought to the surface. Scale and thermal expansion corrections are usually applied to these readings.

Thermographic equipment, usually self-contained recording devices, are used for measuring and recording temperature in water bodies at any desired depth. They are usually left in place for periods of time (several weeks) and retrieved at regular intervals. Thermographs require calibration before and after use.

3.1.2 Taste and Odour

Disagreeable tastes and odours in water are associated with the presence of any of a great variety of living microorganisms or decaying vegetation. Problems of both taste and odour are very complex because the senses of smell and taste are intimately related and their responses are often difficult to differentiate clearly. However, certain non-valatile substances dissolved in water can cause taste without forming odours.

The sense of taste results mainly from chemical stimulation of sensory nerve endings in papillae located on the tonque. Fundamental sensations of taste are, by salt, sweet, bitter and sour. Potable water is analysed to estimate its acceptability for public consumption rather than to assess the taste sensations it produces. Taste and odour differ in the nature and location of the receptor nerve site; high in the nasal cavity for odour, and primarily on the tonque for taste. The odour sensation is stimulated by vapours without physical contact with a water sample, while taste requires contact of the taste buds with the water. Dissolved inorganic salts of copper, iron, manganese, potassium, sodium and zinc can be detected by taste. Concentrations producing taste range from a few tenths of several hundred milligrams per liter.

Odour, like taste, depends on contact of stimulating substance with the appropriate human receptor cell. In its pure form, water cannot produce odour or taste sensations. Odour is recognized as a quality factor affecting acceptability of drinking water, tainting of fish and other aquatic organisms, and esthetics of recreational waters. Most organic and some inorganic chemicals contribute taste or odour. These chemicals may originate from municipal and industrial waste discharge, from natural sources such as decomposition of vegetable matter, or from associated microbial activity.

Some substances, such as certain inorganic salts, produce taste without odour. Many other sensations ascribed to the sense of taste actually are odours, even though the sensation is not noticed until the material is taken in to the mouth. The ultimate odour-testing device is the human nose. Odour tests are performed to provide qualitative descriptions and approximate quantitative measurements of odur intensity. The method for intensity measurement is the threshold odour test, based on the method of limits (American Society for Testing and Materials Committee, 1968).

3.1.3 Colour

Colour in water may result from the presence of natural metallic ions, humus and peat materials, plankton, weeds and industrial wastes. Colour removal is necessary for some industrial processes and is practiced for water intended for general domestic purposes.

Colour may be expressed as 'apparent' or 'true' colour. The apparent colour includes that from dissolved materials plus that from suspended matter. By centrifuging or filtering out the suspended materials, the true colour can be determined.

Principle

Colour is determined by comparison of the sample with known concentrations of coloured solutions. The platinum-cobalt method of measuring colour is the standard method, the unit of colour being that produced by 1 mg platinum/L in the form of chloroplatinate ion.

Interference

Even a slight turbidity causes the apparent colour to be noticeable higher than the true colour, therefore remove turbidity before approximating true colour by differential reading with different colour filters.

The colour value of water is extremely pH-dependent and invariably increases as the pH of the water is raised. Therefore, specify the pH at which colour is determined.

Reagents

i) Potassium chloro platinate

ii) Cobaltous chloride

Procedure

i) Preparation of stock colour standard: Dissolved 1.246 g potassium chloroplatinate, K_2PtCl_6(equivalent to500 mg metallic Pt) and 1.00 g crystallized cobaltous chloride, $CoCl_2.6H_2O$ (equivalent to about 250 mg metallic Co) in distilled water with 100 mL conc HCl and dilute to 1000 mL with distilled water. This stock standard has a colour of 500 units.

ii) Prepare standards having colours of 5,10,15,20,25 30,35,40,45,50,60 and 70 by diluting 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0 and 7.00 mL stock colour standard with distilled water to 50 mL in nessler tubes.

iii) Observe sample colour by filling a matched nessler tube to the 50 mL mark with sample and comparing it with standards. Look vertically downward through tubes toward a white or specular surface placed at such an angle that light is reflected upward through the columns of liquid. If the colour exceeds 70 units, dilute sample with distilled water in known proportions untill the colour is within the range of the standards.

Calculations

$$\text{Colour, PCU} = \frac{A \times 50}{B}$$

where,

A = Estimated colour of a diluted sample, and

B = Sample taken for dilution, mL.

Reporting

Units.................	PCU (Platinum-cobalt units).
Form(s)...............	Colour (true).
Significant figures...	1-50,nearest 1 unit; 51-100, nearest 5 units; 101-250, nearest 10 units; 250-500, nearest 20 units.

3.1.4 Conductivity

Conductivity is a measurement of water's capacity for conveying electrical current and is directly related to the concentrations of ionized substance in the water. Solutions of most inorganic acids, bases and salts are relatively good conductors. Conductivity measurements are commonly used to determine the purity of demineralized water and total dissolved solids in boiler and cooling tower water.

Principle

Specific conductance is a measure of the total concentration of ionised constituents of water. It is related to the sum of anions and cations. Specific conductance is reciprocal of the resistance between 2 electrodes 1 cm apart and 1 Sq. cm in cross section.

Reagents

i) Conductivity water: Pass distilled water through a mixed bed deionizer and discard first liter. Conductivity should be less than 1μmho/cm.

ii) Standard potassium chloride solution, 0.01 N: Disslove 745.6 mg anhydrous KCl in conductivity water and dilute to 1000 mL at 25°C. This is the standard reference solution, which at 25°C has a conductivity of 1413 μ mho/cm. It is satisfactory for most samples when the cell has a constant between 1 and 2.

Procedure

i) Determination of cell constant: Rinse conductivity cell with at least three portions of 0.01 N KCl solution, adjust temperature of a fourth portion to 25.0 ± 0.1°c. Measure resistance of this portion and note temperature. Compute cell constant, C, using following equation:

$$C = (0.001\ 413)\ (R_{KCl}) = 1 + 0.0191\ (t-25)$$

where,

R_{KC1} = measured resistance, ohm , and
t = observed temperature, °C

ii) Conductivity measurement: Rinse cell with one or more portions of sample. Adjust temperature of a final portion to 25.0 ± 0.1°C Measure sample conductivity and note temperature.

Calculation

$$\text{Conductivity at } 25°\text{C}, \mu\text{mho/cm} = \frac{K_m \times C}{1+0.0191(t-25)}$$

where,

K_m = measured conductivity, μ mho at t°c

C = cell constant, cm^{-1} and

t = temperature of measurement.

Reporting

Units......................μmho/cm at 25°C.

Form(s)....................Conductance, specific.

Significant figure.........Less than 100μmho/cm, nearest whole number; 100μmho/cm to 500 μ mho/cm, nearest 5μmho/cm; 500 μmho/cm to 1,000 μmho/cm, nearest 10μmho/cm; above 1,000 μmho/cm, three significant figures.

3.1.5 Solids

Solids refer to matter suspended or dissolved in water or waste water. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatabiltiy and may induce an unfavourable physiological reaction in the transient consumer. For these reasons, a limit of 500mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing.

Total solids is the material residue left after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes total suspended solids and total dissolved solids.

Fixed solids is the residue of total, suspended, or dissolved solids after ignition for a specified time at a specified temperature. The weight loss on ignition is called volatile solids. Determination of fixed and volatile solids do not ditinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts.

3.1.5.1 Total solids

Principle

A Well mixed sample is evaporated in a weighted dish and dried to constant weight in an oven at 103 to 105°C. The increase in weight over that of the empty dish represents the total solids.

Interference

Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

Procedure

Take a known volume of a well mixed sample in constant weight disn. Evaporate to dryness in an oven at 103 to 105°C and dry to a constant weight. Cool the dish in a dessicator. Weigh and note the increase in weight.

Calculation

$$\text{Total solids,mg/L} = \frac{\text{Increase in weight, mg x 1000}}{\text{Volume of sample, mL}}$$

Reporting

Units....................mg/L.

Form(s)..................solids,total.

Significant figures.......Less than 1,000 mg/L nearest whole number;1,000 mg/L and above, three significant figures.

5.1.5.2 Total dissolved solids

Principle

A well mixed sample is filtered throught a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids.

Interference

Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and prolonged drying at 180°C to ensure complete conversion of bicarbonate to carbonate.

Procedure

Filter a known volume of well mixed sample througt glass fiber filter, wash with three successive 10 mL volume of distilled water, and continue suction for about 3 min after filtration is complete. Transfer filtrate to a weighted evaporating dish and evaporate to dryness on a steam bath. Dry for at least one hour in an oven at 180 ± 2°C, cool in a desiccator and weigh to a constant weight. Note the increase in weight.

Calculation

$$\text{Total dissolved solids, mg/L} = \frac{\text{Increase in weight, mg} \times 1000}{\text{Volume of sample, mL}}$$

Reporting

Units..................mg/L.
Form(s)...............Solids, dissolved.
Significant figures...Less than 1,000 mg/L, nearest whole number; 1000 mg/L and above, three significant figures.

5.1.5.3 Total suspended solids

Principle

A well mixed sample is filtered through a weighed standard glass fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids.

Interference

Large floating particles or submerged agglomerates of nonhomogeneous materials are the the prime source of interference They should be excluded from the sample.

Procedure

Filter a known volume of well mixed sample through a glass fiber, wash with three successive 10 mL volume of distilled water, and continue suction for about 3 min after filtration is complete.Carefully remove filter from filteration apparatus and transfer to an aluminum or stainless steel planchet as a support. Dry for at least 1 h at 103 to 105°C in an oven, cool in a desiccator and weigh to a constant weight. Note the increase in weight.

Calculation

$$\text{Total suspended solids, mg/L} = \frac{\text{Increase in weight, mg} \times 1000}{\text{Volume of sample, mL}}$$

Reporting

Units....................mg/L.

Form(s)..................solids,suspended.

Significant figures.......Lessthan 1,000 mg/L,nearest whole number; 1,000 mg/L and above, three significant figures.

3.1.5.4 Fixed and volatile solids

Principle

The residue obtained from method,3.1.5.1, 3.1.5.2 and 3.1.5.3 is ignited to constant weight at 550 ± 50°C. The remaining solids represent the fixed total, dissolved, or suspended solids while the weight loss on ignition is the volatile solids.

Interference

Negative errors in the volatile solids may be produced by loss of volatile matter during drying.

Procedure

Ignite residue produced in earlier methods in a muffle furnace at a temperature of 550 ± 50°C for 15 to 20 minutes. Let dish cool partially in air until most of the heat has been dissipated. Transfer to a desiccator for final cooling in a dry atmosphere and weigh to a constant weight.

Calculation

$$\text{Volatile solids, mg/L} = \frac{(A - B) \times 100}{\text{Volume of sample, mL}}$$

$$\text{Fixed solids, mg/L} = \frac{(B - C) \times 100}{\text{Volume of sample, mL}}$$

where,

A = weight of residue + dish before ignition, mg

B = weight of residue + dish after ignition, mg, and

C = weight of dish, mg.

Reporting

Units...............mg/L.

Form(s) ....Solids, volatile.

Significant figures..Less than 1,000, nearest whole number; 1,000 and above, three significant figures.

3.1.6 Turbidity

Clarity of water is important in producing products destined for human consumption and in many manufacturing uses. The clarity of a natural body of water is a major determinant of the condition and productivity of that system.

Turbidity in water 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. 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.

Principle

This method is based on a comparision 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.

Interference

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

Reagents

i) Solution I : Dissolved 1.0 g hydrazine sulphate in distilled water and dilute to 100 mL in a volumetric flask.

ii) Solution II : Dissolved 10.0 g hexamethylenetetramine in distilled water and dilute to 100 mL in a volumetric flask.

iii) Standard turbidity suspension: In a 100 mL volumetric flask add 5.0 mL solution I and 5.0 mL solution II. Let stand for 24 h at 25 ± 3°C, dilute to mark and mix again. The turbidity of this suspension is 400 NTU. Dilute portions of standard turbidity suspension with turbidity free water as required.

Procedure

i) Follow the manufacturer's operating instructions for calibration of the instrument.

ii) Thoroughly shake sample, wait until air bubbles disappear and pour sample into turbidity meter tube.

iii) Read turbidity directly from instrument scale or from appropriate calibration curve.

iv) For high turbid samples, dilute sample with one or more volume of turbidity free water. Compute turbidity of original sample from tubidity of diluted sample and the dilution factor.

Calculation

$$\text{Turbidity, NTU} = \frac{A \times (B + C)}{C}$$

where,

A = NTU found in diluted sample,

B = Volume of dilution water, mL, and

C = Sample volume taken for dilution, mL.

Reporting

Units..................	NTU.
Form(s)................	Turbidity.
Significant figures.....	1 to 10 NTU, nearest 0.1 NTU; 10 to 40 NTU, nearest 1 NTU; 40 to 100 NTU, nearest 5 NTU; 100 to 400 NTU, nearest 10 NTU; 400 to 1,000 NTU, nearest 50 NTU; greater than 1,000 NTU, nearest 100 NTU.

3.2 Inorganic Non-Metallic Parameters

3.2.1 pH

The pH value is a measure of hydrogen ion concentration and is the negative exponent of the logarithm of the hydrogen ion concentration. A low pH solution has a high hydrogen ion concentration and is therefore, acidic while high pH solution are low in hydrogen ion concentration and are alkaline (pH 7 being neutral).

The pH value of natural water is an important index of acidity or alkalinity and is the resulting value of the acidic/basic interaction of a number of its mineral and organic components. In pure or slightly polluted water, the value of pH are determined mainly by the correlation between the concentrations of free carbon dioxide, bicarbonate and carbonate ions. This correlation, in turn depends substantially on the intensity of the process of photosynthesis and the biochemical oxidation of organic substances as well as on chemical conversions of some mineral substances.

Most natural water range from pH 4 to 9 and are often slightly basic due to the presence of carbonates and bicarbonates. A major deviation from the normal pH for a given water indicates the industrial wastes. Practically every phase of water supply and wastewater treatment, e.g., acid- base neutralization, water softening, precipitation, coagulation, disinfection, and corrosion control, is pH dependent.

The pH value of water may be determined potentiometrically by a wide variety of pH meters which are battery operated or run by standard-line power. They are equipped with glass and reference electrodes which require standardizing with standard buffer solutions before each measurement in the field. Care must also be taken that the pH meters are stored in a dry place to prevent them from getting wet.

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 eletrode across which hydrogen gas a 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 exchanged 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.

$$pH = - \log [H^+]$$

Interference

The glass electrode is relatively free from inteference from colour, turbidity, colloidal matter, oxidants, reductantts, or high salinity, except for a sodium error at $pH > 10$. This error can be reduced by using special 'low sodium error' electrodes. Other source of interference is temperature.

Reagents

i) Potassium hydrogen phthalate, 0.05M : Dissolved 10.12 g potassium hydrogen phthalate in 1L of distilled water at 25°C.

ii) Sodium borate deca hydrate, 0.01 M : Dissolve 3.80g sodium borate deca hydrate in 1L of distilled water at 25°C.

Procedure

i) For detailed instructions, follow manufacturer's manual, Standardise the pH meter by immersing the electrode in buffer solution of known pH. Read the pH and correctly adjust with the control untill the meter indicates the correct value for pH of buffer solution.

ii) Remove electrodes from first buffer, rinse thoroughly with distilled water, blot dry with a soft tissue, and immerse in second buffer, the reading should be within 0.1 unit for the pH of the buffer. If the response shows a difference greater than 0.1 pH unit from expected value, look for trouble with the electrode or pH meter.

iii) Rinse the electrodes in distilled water and immerse them in the sample. Let the reading stabilize. Read the pH value.

Reporting

Units................pH.

Form(s).............pH.

Significant figures......Report to the nearest 0.1 pH unit.

3.2.2 Acidity

Acidity is a quantitative expression of a water's capacity to neutralize a strong base to a designated pH. The amount of acidity indicates the water's degree of corrosiveness and influence chemical reaction rates, chemical speciation and biological processes.

Acidity is caused by weak organic acid such as carbonic, acetic or tannic acids, or by strong mineral acids such as sulfuric or hydrochloric.

Principle

Hydrogen ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard alkali. Acidity thus depends on the end point pH or indicator used. In non-polluted water the acidity is due primarily to dissolved carbon dioxide which can be neutralized by titrating to its neutraliztion point at pH 8.3. For systems which are more complex (such as industrial wastes or buffered solutions) a pH of 4.5 has been arbitrarily chosen and gives an estimate of the strong mineral acids present.

Interference

Colour, turbidity, iron, alluminium and residual chlorine are prime sources of interference.

Reagents

i) Methyl orange indicator: Dissolve 0.5 g of methyl

ii) Phenolphthalein indicator: Dissolve 5.0 g phenolphthalein in 1L of 5.0% ethyl alchol, neutralize the solution with 0.02 N NaOH solution.

iii) Sodium hydroxide solution, 0.02 N: dissolve 4.0 g of dried sodium hydroxide pellets in 1L of distilled water. Standardise the solution against 0.1 N H_2SO_4 using methyl orange as indicator. Dilute this solution by adding distilled water to give 0.02 N NaOH solution.

Procedure

i) Take 100 mL sample in a conical flask and add to it 2 drops of methyl orange indicator and swirl to mix.

ii) If it gives an orangish red colour it means mineral acidity is available. Titrate it with sodium hydroxide standard solution, 0.02 N, to a yellow end point. Note the volume of NaOH used.

iii) In another flask take 100 mL sample and add 2-3 drops phenolphthalein indicator. If it does not give any colour, titrate with sodium hydroxide standard solution, 0.02 N, to a pink end point. Note the volume of sodium hydroxide solution used.

iv) If phenolphthalein gives a pink colour on addition in the sample, acidity is not available.

Calculation

$$\text{Mineral acidity mg/L as } CaCO_3 = \frac{A \times 1000}{\text{Volume of sample, mL}}$$

$$\text{Carbonate acidity, mg/L as } CaCO_3 = \frac{A \times 1000}{\text{Volume of sample, mL}}$$

where,

A = Volume of NaOH solution used with methyl orange indicator, mL, and

B = Volume of NaOH solution used with phenolphthalein indicator, mL.

Reporting

Units..................mg/L.

Form(s)................Acidity, as $CaCO_3$.

Significant figures.....Less than 200 mg/L, nearest whole number; 200 mg/L and above, two significant figures.

3.2.3 Alkalinity

Alkalinity refers to the capability of water to neutralize acids. The presence of carbonates, bicarbonates and hydroxides is the most common cause of alkalinity in natural waters. Alkalinities values provide guidance in applying proper doses of chemicals in water and waste water treatment processes, particularly in coagulation, softening and operational control of anaerobic digestion.

Bicarbonates present the major form since they are formed in considerable amounts from the action of carbonate upon the basic materials in the soil.

$$CO_2 + CaCO_3 + H_2O = Ca(HCO_3)_2$$

Natural waters may also contain appreciable amounts of carbonates and hydroxide alkalinities, particularly surface waters blooming with algae. The algae take up carbonate for its photosynthesis activities and raise the pH.

Principle

Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end point pH used. Alkalinity can be obtained by neutralizing hydroxide, carbonate and bicarbonate with standard sulfuric acid solution. Titration to pH 8.3 or de-colouration of phenolphthalein indicator will snow complete neutralization of total hydroxide and one half the carbonate present, while to pH 4.4 or sharp change from yellow to pink colour of methyl orange indicator will indicate total alkalinity, i.e. hydroxide, carbonate and bicarbonate.

Interference

Colour, turbidity, iron, aluminium and residual chlorine are prime sources of interference.

Reagents

i) Methyl orange indicator : Dissolve 0.5 g of methyl orange in 1 L of distilled water.

ii) Phenolphthalein indicator: Dissolve 5.0 g phenolphthalein in 1 L of 5.0% ethyl alchol. Neutralize the solution with 0.02 N NaOH solution.

iii) Sulfuric acid,0.02 N: Prepare stock H_2SO_4 solution (approximately 0.1N) by diluting 3 ml H_2SO_4 to 1 L of distilled water. Dilure 200 mL of the 0.1 N stock solution to 1 L with distilled water. Standardise the 0.02 N acid against 0.02 N sodium carbonate solution.

Sodium carbonate solution can be made by dissolving 1.06 g of Na_2CO_3 oven dried, in 1 L of distilled water. The standardisation is done by titrating exactly like an alkalinity titration using phenolphthalein or methyl orange as indicator.

Procedure

i) Take 100 mL sample in a conical flask and add 2-3 drops of phenolphthalein indicator and swirl to mix.

ii) If pink colour develops titrate the sample with sulfuric acid standard solution, 0.02 N, while swirling the flask until the solution changes from pink to colourless or the pH meter reads 8.3. Note the volume of sulfuric acid required.

iii) Add 2-3 drops methyl orange indicator to the titrated solution and swirl to mix. Continue titration with sulfuric acid standard solution, 0.02 N, to a pink colour or pH comes down to 4.5. Note the volume of sulfuric acid used.

iv) In case pink colour does not appear after addition of phenolphthalein continue as in 3 above.

Calculation

Total (T) , phenolphthalein(P) and methyl orange (MO) alkalinity can be calculated as follows:

$$\text{P alkalinity, mg/L as } CaCO_3 = \frac{A \times 1000}{\text{Volume of sample, mL}}$$

$$\text{MO alkalinity,mg/L as } CaCO_3 = \frac{B \times 1000}{\text{Volume of sample,mL}}$$

$$\text{T alkalinity,mg/L as } CaCO_3 = \frac{(A + B) \times 1000}{\text{Volume of sample, mL}}$$

where,

A = volume of sulfuric acid used with phenolphthalein indicator, mL, and

B = Volume of sulfuric acid solution used with methyl orange indicator, mL .

Calculate OH, CO_3 and HCO_3 forms from the valves of P and T as follows:

Values of P & T	OH	CO_3	HCO_3
P = O	O	O	T
$P < 1/2$ T	O	2P	T-2P
P =1/2 T	O	2P	O
$P > 1/2$ T	2P-T	2(T-P)	O
P = T	T	O	O

Reporting

Units..................mg/L.

Form(s)................Alkalinity, as $CaCO_3$.

Significant figures....Less than 1,000 mg/L, nearest whole number;1,000 mg/L and above, three significant figures.

3.2.4 Hardness

The Hardness of water was orginally defined in terms of its ability to precipitate soap. Calcium and magnesium ions are the principle causes although iron, aluminium, manganese, strontium, zinc and hydrogen ions are capable of producing the same effect. High concentrations of the latter ions are not commonly found in natural waters. In confirmity with current practice, total hardness is defined as characteristic of water which represents the total concentration of calcium and magnesium expressed as their calcium carbonate equivalent.

Temporary hardness is caused by the presence of bicarbonates of calcium and magnesium. Permanent hardness is mostly due to sulfates.

When the total hardness has a value greater than total alkalinity, the amount of hardness equivalent to the alkalinity is called carbonate hardness and the excess amount is non carbonate hardness. When total hardness is equal or less than the total alkalinity, there is no carbonate hardness.

Principle

Ethylenediaminetetracetic acid and its sodium salts (abbreviated EDTA) form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of dye such as Eriochrome black T is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0 ± 0.1, the solution becomes wine red. When EDTA is added as a titrant, the calcium and magnesium get complexed resulting in sharp change from wine red to blue which indicates end point of the reaction. Magnesium ion must be present to yield a satisfactory end point. To ensure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer, this automatically introduces sufficient magnesium and obviates the need for a blank correction. At higher pH, i.e., about 12.0 magnesium ion precipitates and only calcium ion remain in solution. At this pH murex indicator form a pink colour with calcium ions. When EDTA is added calcium gets complexed resulting in a change from pink to purple which indicates end point of the reaction.

Interference

Some metal ions do interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA but can be overcome by addition of inhibitors.

Reagent

i) Buffer solution : Dissolve 16.9 g of ammonium chlo- (NH_4Cl) in 143 mL conc ammonium hydroxide (NH_4OH), add 1.25 g magnesium salt of EDTA and dilute to 250 mL with distilled water

If the magnesium salt of EDTA is not available, dissolve 1.179 g disodium salt of ethylenediamine tetraacetic acid dihydrate and 780 mg magnesium sulfate ($MgSO_4.7H_2O$) or 664 mg magnesium chloride ($MgCl_2.6H_2O$) in 50 mL distilled water. Add this solution to 16.9 g NH_4Cl and 143 mL conc NH_4OH with mixing and dilute to 250 mL with distilled water.

ii) Inhibitor: Dissolve 4.5 g hydroxyl amine hydrochloride in 100 mL 95% ethyl alcohol.

iii) Eriochrome black T indicator: Mix 0.5 g dye with 100 g NaCl to prepare dry powder or dissolve 0.1g of eriochrome black T in 20 mL of ethyl alcohcl.

iv) Murex indicator : Dry powder.

v) Sodium hydroxide, 2N : Dissolve 80 g NaOH and dilute to 1 L.

vi) Standard EDTA solution, 0.01 M : Dissolve 3.723g EDTA sodium salt and dilute to 1000 mL. Standardize against standard calcium solution, 1 mL = 1 mg $CaCO_3$.

vii) Standard calcium solution : Weigh accurately 1.0g anhydrous $CaCO_3$ powder into a 500-mL erlanmeyer flask. Place a funnel in the flask neck and add 1 + 1 HCL till $CaCO_3$ dissolves completely. Add 200 mL distilled water and boil for a few minutes to expel CO_2. Cool and add a few drops of methyl red indicator and adjust to the intermediate orange colour by adding 3N NH_4OH or 1+1 HCL. Dilute to 1000 mL to obtain 1 mL - 1 mg $CaCO_3$.

Procedure

i) Take 100 mL water sample in a conical flask and add to it 1-2 mL buffer solution followed by 1 mL inhibitor.

ii) Add 2 drops eriochrome black T indicator and titrate with standard EDTA solution, 0.01 M, till wine red colour changes to blue. Note the volume of EDTA used.

iii) In another flask take 100 mL sample and add 1 mL sodium hydroxide solution to raise the pH to 12.0 and a pinch of murex indicator.

iv) Titrate with standard EDTA solution, 0.01M, till pink colour changes to purple. Note the volume of EDTA used .

Calculation

$$\text{Total hardness, mg/L} = \frac{A \times C \times 1000}{\text{Volume of sample, mL}}$$

$$\text{Calcium hardness,mg/L} = \frac{B \times C \times 1000}{\text{Volume of sample, mL}}$$

Magnesium hardness, mg/L = Total hardness - Calcium hardness

where,

A = Volume of EDTA solution used with eriochrone black T indicator, mL,

B = Volume of EDTA solution used with murex indicator, mL, and,

C = mg $CaCO_3$ equivalent to 1.0 mL EDTA titrant.

Reporting

Units	mg/L.
Form(s)	Hardness, as $CaCO_3$
Significant figures	Less than 10 mg/L, nearest whole number; 10 mg/L and above, tow significant figures.

3.2.5 Sulfate

Sulfate appears in natural waters in a wide range of concentrations. Mine waters and industrial effluents frequently contain large amounts of sulfate from pyrite oxidation and the use of sulfuric acid. Sodium and magnesium sulfate exert cathertic action and hence its concentration above 250 mg/L in potable water is objectionable. Sulfate cause a problem of scaling in industrial water supplies, and problem of odour and corrosion in waste water treatment due to its reduction to hydrogen sulfide.

Principle

Sulfate ions are precipated in acetic acid solution with barium chloride so as to form a uniform suspension of barium sulfate crystals. The absorbance of the suspension is measured by a photometer and the sulfate concentration is determined by comparison of the reading with a standard curve.

Interference

Colour and suspended matter in large amounts will interfere. Some suspended matter may be removed by filtration. Silica in excess of 500 mg/L interfere.

Reagents

i) Buffer Solution : Dissolve 30 g magnesium chloride, $MgCl_2.6H_2O$, 5 g sodium acetate, $CH_3COONa.3H_2O$, 1.0 g potassium nitrate, KNO_3, and 20 mL acetic acid, CH_3COOH(99%), in 500 mL distilled water and make up to 1000mL.

ii) Barium chloride crystals : 20 to 30 mesh.

iii) Standard sulfate solution : Dissolve 0.147 g of anhydrous Na_2SO_4 in distilled water and dilute to 1000 mL, 1.00 mL = 100 µg SO_4^{2-}.

Procedure

i) Take 100 mL sample, or suitable portion made upto 100 mL, into a 250 mL flask. Add 20 mL buffer solution and mix in stirring apparatus. Add berium chloride crystals while stirring. Continue stirring for 1 minute after addition of barium chloride.

ii) Measure the turbidity developed after five minutes on colorimeter at 420 nm.

iii) Prepare standard curve by carrying standard sulfate solution through entire procedure. Space standards at 5 mg/L increment in the 0 to 40 mg/L range. Above 40 mg/L accuracy decreases and barium sulfate suspension loss stability.

iv) Read the concentration of sulfate present in the sample from the standard curve.

Calculation

$$\text{Sulfate, mg/L} = \frac{\text{mg } SO_4^{-2} \times 1000}{\text{Volume of sample, mL}}$$

Reporting

Units......................mg/L .
Form(s)...................Sulphate ion (SO_4^{2-}) ,dissolve
Significant figures.......10 to 100 mg/L, nearest mg/L; 100 mg/L and above, two significant figures.

3.2.6 Chloride

Chloride, in the form of chloride ion, is one of the major inorganic anions in water and waste water. Chlorides are present in all potable water supplies and in sewage, usually as a metallic salt. When sodium is present in drinking water, chloride concentrations in excess of 250 mg/L give a salty taste. If the chloride is present as a calcium or magnesium salt, the taste detection level may be as high as 1000 mg/L chloride.

Chloride is essential in the diet and passes through the digestive system unchanged to become one of the major components of raw sewage. The wide use of zeolite in water softeners also contribute a large amount of chloride to sewage and waste waters.

High chloride concentrations in water are not known to have toxic effects on man, though large amounts may act corrosively on metal pipes and be harmful to plant life. The maximum allowable chloride concentration of 250 mg/L in drinking water has been established for reasons of taste rather than as a safeguard against physical hazard.

Principle

In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromete is formed.

Interference

Bromide, iodide, Cyanide, Sulfide, thiosulfate, sulfite, iron, phosphate are prime sources of interference.

Reagents

i) Potassium chromate indicator : Dissolve 50 g of potassium chromate in a small quantity of distilled water. Add $AgNO_3$ solution to produce a light red precipitate. Allow to stand overnight and filter. Make up to 1 L.

ii) $\frac{N}{35.5}$ Silver nitrate solution : Disslove 4.78 g of silver nitrate in 1 L of distilled water. Standardise with standard sodium chloride solution.

Procedure

i) Take 100 mL sample in a conical

flask. If the sample is highly coloured, add 3 mL aluminum hydroxide suspension, mix well, allow to settle and filter. If sulfide, sulfite or thiosulfate is present, add 1 mL hydrogen peroxide and stir for 1 minute.

ii) Adjust the pH of sample between 7.0 and 10.0 if it is not in this range and add 1.0 mL potassium chromate indicator solution.

iii) Titrate with standard silver nitrate solution, N/35.5, to a pinkish yellow end point. Note the volume of silver nitrate solution used.

iv) Place the same quantity of chloride free distilled water in another flask and establish reagent blank value by the titration method outlined above.

Calculation

$$\text{Chloride, mg/L} = \frac{(A - B) \times 1000}{\text{Volume of sample, mL}}$$

where,

A = Volume of $AgNO_3$ used for sample, mL, and

B = Volume of $AgNO_3$ used for blank, mL.

Reporting

Units....................mg/L.

Form(s)..................Chloride ion (Cl^-).

Significant figures.......Less than 10 mg/L, one decimal place; 10 mg/L and above, two significant figures.

3.2.7 Fluoride

Fluoride occurs naturally in some ground waters and a 1 mg/L level normally is maintained in public drinking water supplies for the prevention of dental carries. Excessive amounts of fluoride cause an objectionable discoloration to tooth enamel called fluorosis, although levels upto 8 mg/L have not been found to be physiological harmful.

Accurate determination of fluoride has increased in importance with the growth of the practice of fluoridation of water supplies as a public health measure. Maintenance of an optimal fluoride concentration is essential in maintaining effectiveness and safety of fluoridation procedure.

Principle

Under acid condition fluorides react with zirconium SPADN solution and the lake colour of SPADN reagent gets bleached due to formation of ZrF_6. Since bleaching is a function of fluoride ions, it is directly proportional to the concentration of fluoride.

Interference

Alkalinity 5000 mg/L, aluminium 0.1 mg/L, chlorides 7000 mg/L, iron (ferric) 10 mg/L, phosphate (ortho) 16 mg/L,sulfate 200 mg/L and sodium hexametaphosphate 1.0 mg/L interfere in the bleaching action. In preference of interfering radicals distillation of sample is recommended.

Reagents

i) Stock fluoride solution : Dissolve 221.0 mg anhydrous sodium fluoride, NaF, in distilled water and dilute to 1000 mL; 1.000mL = 100 ugF$^-$.

ii) Standard fluoride solution : Dilute 100 mL stock fluoride solution to 1000 mL with distilled water; 1.00 mL = 10.0 $\mu g F^-$.

iii) SPADNS solution : Dissolve 958 mg SPADNS, sodium 2-(parasulfophenylazo) -1, 8-dihydroxy-3, 6-naphthalene disulfonate also called 4,5 -dihydroy -3-(parasulfophenylazo)-2, 7-naphthalene disulfonic acid trisodium salt, in distilled water and dilute to 500 mL. This solution is stable for atleast. 1 year if protected from direct sunlight.

iv) Zirconyl-acid reagent : Dissolve 133 mg zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$, in about 25mL distilled water. Add 350 mL conc HCl and dilute to 500 mL with distilled water.

v) Acid zirconyl-SPADNS reagent : Mix equal volumes of SPADNS solution and zirconyl acid reagent. The combined reagent is stable for atleast 2 years.

vi) Reference solution : Add 10 mL SPADNS solution in 100 mL distilled water. dilute 7 mL conc HCl to 10 mL and add to the diluted SPADNS solution. the resulting solution, used for setting the instrument reference point (zero), is stable for at least 1 year. Alternatively, use a prepared standard of 0 mg F^-/L as a reference.

vii) Sodium arsenite solution : dissolve 5.0 g $NaAsO_2$ and dilute to 1 L with distilled water.

Procedure

i) Prepare fluoride standards in the range of 0 to 1.40 mg F^-/L by diluting appropriate quantities of standard fluoride solution to 50 mL with distilled water. Pipet 5.0mL each of SPADNS solution and zirconyl-acid reagent, or 10 mL mixed acid-zirconyl-SPADNS reagent, to each standard and mix well. Set photometer to zero absorbance with reference solution at 570nm and obtain absorbance reading of standards. Plot a curve of the milligrams fluoride - absorbance relationship.

ii) If the sample contains residual chlorine, remove it by adding 1 drop (0.05mL) sodium arsenite solution/0.1 mg residual chlorine and mix. Sodium arsenite concentration of 1300mg/L produce an error of 0.1 mg F^-/L.

iii) Use 50 mL sample or a portion diluted to 50 mL with distilled water. Add 5.0 mL each of SPADNS solution and zirconyl-acid reagent, or 10.0 mL acid-zirconyl-SPADNS reagent, mix well and read absorbance, first setting the reference point of the photometer as above.

Calculation

$$\text{Flouride, mg/L} = \frac{\text{mg } F^- \text{ in aliquot} \times 1000}{\text{Volume of sample, mL}}$$

Reporting

Units....................mg/L.

Form(s)..................Fluoride ion(F^-), dissolved.

Significant figures......Less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

3.2.8 Dissolved Oxygen

Dissolved oxygen (DO) levels in natural and waste waters depends on the physical, chemical and biochemical activities in the water body. The analysis for DO is a key test in water pollution and waste treatment process control. The effect of oxidation on streams, the suitability of water fish and other organisms, and the progress of self-purification can all be measured or estimated from the dissolved oxygen contents. In aerobic sewage treatment units, the minimum objectionable odour potential, maximum treatment efficiency and stabilization of waste water are dependent on maintenance of adequate dissolved oxygen.

Principle

It is based on the addition of divalen manganese solution, followed by strong alkali, to the sample in the glass stoppered bottle. dissolved oxygen rapidly oxidizes an equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxide of higher valency states. In the presence of iodide ion in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content. The iodine is then titrated with a standard solution of thiosulfate, using starch as an indicator.

Interference

Ferrous ion, ferric ion, nitrite microbial mass and high suspended solids constitute the main source of interference. Modifications in the estimation procedure to reduce these interference are as follows:

a. Alsterberg azide modification : The azide modification effectively removes interference caused by nitrite, which is the most common interference in biologically treated effluents and incubated BOD samples. The reagent alkali-iodide-azide is used in the method to eliminate interference caused by nitrite.

b. Permanganate modification : This modification is used when the sample contain ferrous ion. Add 0.7 mL conc. sufuric acid followed by 1 mL 0.63% potassium permanganate immediately after collection in the BOD bottle itself. It ferric ions are present in large conc add 1 mL of 40% potassium fluoride solution. Remove excess potassium permanganate using potassium oxalate just sufficient to neutralise potassium permanganate as excess oxalate give negative error.

c. Alum flocculation modification: Samples high in suspended solids may consume appreciable quantities of iodine in acid solution. The interference due to solids may be removed by alum flocculation by adding 10 mL of 10% alum solution followed by 1-2 mL of conc ammonium hydroxide to 1000 mL of the sample. Allow to settle for 10 minutes and siphon the clear supernatant for DO estimation.

d. Copper sulfate sulfamic acid flocculation modification: Activated sludged contain biological flocs having high demand for oxygen. Samples from such treatment plants are fixed by adding 10 mL copper sulfate sulfamic acid reagent to 1000 mL of the sample. The reagent is prepared by adding 32 g sulfamic acid to 475 mL distilled water + 50 g copper sulfate in 500 mL distilled water + 25 mL acetic acid.

Reagents

i) Manganous sulfate solution : Dissolve 480 g $MnSo_4.4H_2O$ or 400 g $MnSO_4.2H_2O$ or 364 g $MnSO_4.H_2O$ in distilled water, filter, and dilute to 1 L. The $MnSO_4$ solution should not give a colour with starch when added to an acidified potassium iodide (KI) solution.

ii) Alkali-iodide-azide reagent : Dissolve 500 g NaOH (or 700 g KOH) and 135 g NaI(or 150 KI) in distilled water and dilute to 1 L. Add 10g NaN_3 dissolved in 40 mL distilled water. Potassium and Sodium salts may be used interchangeably.

iii) Conc sulfuric acid

iv) Starch indicator : Dissolve 2g laboratory grade soluble starch and 0.2 g salicylic acid, as a preservative, in 100 mL hot distilled water.

v) Sodium thiosulfate solution, 0.025N : Dissolve 6.205 g $Na_2S_2O_3.5H_2O$ in boiled cooled distilled water and dilute to 1000 mL. Preserve by adding 5 mL chloroform per litre (This solution will have to be standardized for each set of titrations).

Procedure

i) Collect the sample in a BOD bottle taking care to avoid contact of sample with air. It is always perferably to collect the sample through a sampler.

ii) Add 1.0 mL of manganous sulfate solution followed by 1.0 mL alkali-iodide-azide reagent. If pipets are dipped into sample, rinse then before returning them to reagent bottles. Insert the stopper and mix throughly.

iii) When precipitate has settled sufficiently (to approximately half the bottle volume) to leave clear supernate above the manganese hydroxide floc, add 1.0 mL conc sulfuric acid. Restopper and mix by inverting several times until dissolution is complete.

iv. Titrate a volume corresponding to 200 mL original sample after correction for sample loss by displacement with reagents. Thus, for a total of 2 mL (1 mL each) of manganous sulfate & alkali-iodide-azide reagents in a 300 mL bottle, titrate 200 x 300/(300-2) = 201 mL.

v) Titrate with 0.025 N $Na_2S_2O_3$ solution to a pale straw colour. Add a few drops of starch solution and continue titration to first disappearance of blue colour.

Calculation

1.0 mL of 0.025 N $Na_2S_2O_3$ = 0.2 mg of O_2, the mL of this solution used is equivallent to mg/L of dissolved oxygen.

Reporting

Units.....................mg/L .
Form(s)..................Oxygen(O_2), dissolved.
Significant figures.......One decimal throughout range.

3.2.9 Phosphate

Phosphorous occurs in natural waters and in wastewaters almost solely as phosphates. Phosphates are used widely in muncipal and private water treatment systems and are commonly grouped into three types. Orthophosphate, condensed (pyro, meta or other poly) phosphate, and organically bound phosphate. The orthophosphate is the only form determined directly. The other types require pretreatment for conversion to the orthophosphate form for analysis.

Phosphate enter the water supply from agricultural fertilizer run-off, water treatment, and biological wastes and residues. Industrial effluents related to corrosion and scale control, chemical processing, and the use of detergents and surfactants contribute significantly. Condensed phosphates are the forms commonly used in treating water systems and boilers and in detergent formulations. After being dissolved in water, these are converted to orthophosphates at different rates depending upon their types, the temperature of the water and the pH.

A certain amount of phosphate is essential to organisms in natural water and is often the limiting nutrient for growth. Too much phosphate can produce eutrophication or overfertilization of receiving waters, especially if large amounts of nitrates are present. The result is the rapid growth of aquatic vegetation in nuisance quantities and an eventual lowering of the dissolved oxygen content of the lake or stream due to the depth and decay of the aquatic vegetation.

Principle

In a dilute orthophosphate solution, ammonium molybdate react to form a heteropolyacid, molybdophosphoric acid which is reduced by stannous chloride to intensely coloured molybdenum blue.

Interference

Silica and arsenate causes positive interference. Blue colour is caused by ferrous ion but this does not affect results if ferrous iron concentration is less than 100 mg/L.

Reagents

i) Phenolphthalein, indicator aqueous solution.

ii) Hydrochloric acid : Add 300 mL conc H_2SO_4 to about 600 mL distilled water. When cool, add 4.0 mL conc HNO_3 and dilute to 1L.

iii) Ammonium molybdate reagent : Dissolve 25g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 175 mL distilled water. Cautiously add 280 mL conc H_2SO_4 to 400 mL distilled water. Cool, add molybdate solution, and dilute to 1 L.

iv) Stannous chloride reagent : Dissolve 2.5g fresh $SnCl_2\cdot 2H_2O$ in 100 mL glycerol. Heat in a water bath and stirr with a glass rod to hasten dissolution.

v) Standard phosphate solution : Dissolve 219.5 mg anhydrous KH_2PO_4 in distilled water and dilute to 1000 mL, 1.00 mL = 50µg PO_4^{3-} -P.

Procedure

i) Take 100 mL sample and add one drop phenolphthalein indicator. If sample turns pink, add strong acid solution dropwise to discharge the colour.

ii) Add 4.0 mL ammonium molybdate reagent and 10 drops stannous chloride reagent. A blue colour will develop if phosphate is present. Allow the colour to develop for 10 minutes but no longer than 15 minutes.

iii) Measure colour photometrically at 690 nm and compare with a calibration curve, using a distilled water blank.

Calculation

$$\text{Phosphate,mg/L} = \frac{\text{mg P(in approximately 104.5 mL final volume)x100}}{\text{Volume of sample , mL}}$$

Reporting

Units.....................mg/L.

Form(s)...................Phosphorous (P), orthophosphate, dissolved.

Significant figures.......Less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

3.2.10 Nitrogen

In waters and waste waters the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen. all these forms of nitrogen, as well as nitrogen gas, are biochemically interconvertible and are components of the nitrogen cycle.

Organic nitrogen is defined functionally as organically bound nitrogen in the trinegative oxidation state. It does not include all organic nitrogen compounds. Analytically, organic nitrogen and ammonia can be determined together and have been referred to as 'Kajeldahl nitrogen', a term that reflects the technique used in their determination.

Organic nitrogen includes such natural materials as proteins and peptides, nucleic acids and urea, and numerous synthetic organic materials.

Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen. Nitrate generally occurs in trace quantities in surface water but may attain high levels in groundwater. High levels of nitrate in water indicate biological wastes in the final stages of stabilization or runoff from heavily fertilized fields. Nitrate rich effluents discharged into receiving waters can degrade water quality by encouraging excessive growth of algae. Drinking waters containing excessive amounts of nitrates can cause infant methemoglobinemia (blue babies). For this reason a limit of 10 mg nitrate as nitrogen/L has been established in public drinking water supplies.

Nitrite nitrogen occurs as an intermediate stage in the biological decomposition of compounds containing organic nitrogen. Nitrite-forming bacteria convert ammonia under aerobic conditions to nitrites. The bacterial reduction of nitrates also can produce nitrites under anaerobic conditions. Nitrites are often used as corrosion inhibitors in industrial process water and cooling towers, and the food industry uses nitrite compounds as preservatives.

Ammonia nitrogen is a product of the microbiological decay of plant and animal protein. It can be reused directly by plants and is commonly used in commercial fertilizers. It is present naturally in surface and wastewaters. Its concentration generally is low in groundwaters because it absorbs to soil particles and clays and is not leached readily from soils.

3.2.10.1 Nitrogen, ammonia

Principle

Ammonia produces a yellow coloured compound when treated with alkaline nessler reagent, provided the sample is clarified properly. Pretreatment with zinc sulfate and sodium hydroxide precipitates calcium, iron, magnesium and sulfide and removes turbidity and apparent colour. Addition of EDTA solution prevents precipitation of residual calcium and magnesium in the presence of alkaline Nessler's reagent.

Interference

Colour, turbidity, calcium, magnesium and iron constitute the prime source of interference.

Reagents

i) Zinc sulfate solution : Dissolve 10 g $ZnSO_4.7H_2O$ in distilled water and dilute to 100 mL.

ii) Sodium hydroxide, 6N: Dissolve 24g NaOH and dilute to 100 mL.

iii) EDTA reagent : Dissolve 50g EDTA in 60 mL water containing 10g NaOH. If necessary, apply gentle heat to complete dissolution. Cool to room temperature and dilute to 100 mL.

iv) Rochelle salt solution : Dissolve 50g potassium sodium tartrate tetrahydrate, $K NaC_4H_4O_6 . 4H_2O$, in 100 mL water. Remove ammonia usually prsent in the salt by boiling off 30 mL of solution. After cooling, dilute to 100 mL.

v) Nessler's reagent : Dissolve 100 g HgI_2 and 70 g KI in a small quantity of water and add this mixture slowly, with stirring, to a cool solution of 160g NaOH dissolved in 500 mL water. Dilute to 1L. Store in rubber-stoppered borosilicate glassware and out of sunlight to maintain reagent stability for up to a year under normal laboratory conditions.

vi) Standard ammonia solution : Dissolve 3.819 g anhydrous NH_4Cl, dried at 100°C, in water and dilute to 1000 mL ; 1.00 mL = 1.00 mg N = 1.22 mg NH_3. Dilute 10.0 mL of this solution to 1000 mL with water; 1.00 mL = 10.0 μg N = 12.2μg NH_3.

Procedure

i) Take 100 mL of sample. Add 1 mL zinc sulfate solution and 0.5 mL sodium hydroxide to obtain a pH of 10.5. Allow to settle and filter the supernatant through whatman filter paper No. 42.

ii) Take a suitable aliquot of sample and dilute to 50 mL.

iii) Add 1-2 drops of Rochelle salt solution or 1 drop of EDTA and mix well.

iv) Add 2 mL Nessler's reagent if EDTA is used or 1 mL Nessler's reagent if Rochelle salt is used. Make upto 100 mL.

v) Mix well and read transmittance after ten minutes at 425 nm using a reagent blank prepared in the same way using distilled water instead of sample.

vi) Prepare a calibration curve using suitable aliquots of standard solution of the range of 5 to 120μg/100mL for reference following the same procedure as 1 to 5 but using standard solutions in place of sample.

vii) Read the concentration from the calibration curve.

Reporting

Units....................mg/L.

Form(s)..................Nitrogen, ammonia (NH_3-N).

Significant figures.......Less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

3.2.10.2 Nitrogen, nitrate

Principle

Two mole of nitrate react with one mole of chromotropic acid to form a yellow reaction product with maximum absorbance at 410 nm. The maximum colour develops with 10 min and is stable for 24 h.

Interferences

Residual chlorine, certain oxidants and nitrite yield yellow colours with chromotropic acid. Addition of sulfite eliminates interference from residual chlorine and oxidizing agents. Addition of urea converts nitrite to nitrogen gas.

Reagents

i) Stock nitrate solution : Dissolve 0.721 g dry potassium nitrate, KNO_3 , in water and dilute to 1000 mL. Preserve with 2 mL $CHCl_3$ /L; 1.00 mL = 100µg NO_3^--N.

ii) Sulfite-urea reagent : Dissolve 5 g urea and 4g anhydrous sodium sulfite, Na_2SO_3 , in water and dilute to 100 mL.

iii) Chromotropic acid reagent : Dissolve 100 mg purified chromotropic acid in 100 mL conc H_2SO_4 and store in a brown bottle. A colourless reagent solution signifies the absence of NO_3^- contamination from H_2SO_4.

Procedure

i) Prepare nitrate standards in the range 0.1 to 5.0 mg N/L by diluting 0,1.0,5.0,10,25,40 and 50 mL standard nitrate solution to 100 mL with water.

ii) Pipet 2.0 mL portions of standards, samples and a water blank into dry 10 mL volumetric flasks. Use dilutions of standards and samples in the range 0.1 to 5.0 mg NO_3^- -N/L.

iii) To each flasks add 1 drop sulfite-urea reagent and place flasks in a tray of cold water (10 to 20°C).

iv) After about 5 min. in the bath, add 1 mL chromotropic acid reagent, swirl, and let stand in cooling bath for 3 min. Add conc sulfuric acid to bring volume near the 10mL mark. Stopper flask and mix by inverting each flask four times. Let stand for 45 min at room temperature and adjust volume to 10 mL with conc sulfuric acid.

v) Read absorbance at 410 nm between 15-20 min after last volume adjustment. Use double distilled water in the reference cell.

vi) Read concentration from the calibration curve

Calculation

$$\text{Nitrate nitrogen,mg/L} = \frac{\mu g NO_3^- - N \text{ (in 10 mL final volume)}}{\text{Volume of sample, mL}}$$

Reporting

Units......................mg/L.

Form(s)....................Nitrogen, nitrate (NO_3-N).

Significant figures........Less than 1.0 mg/L,One decimal; 1.0 mg/L and above, two significant figures.

3.2.10.3 Nitrogen, nitrite

Principle

Under acid condition (pH 2.0 to 2.5) nitrite ion as nitrous acid reacts with sulfanilic acid and forms diazonium salt which combines with N-(1-naphthyl)-ethylenediamine dihydrochloride to form pinkish red azo dye. Colour produced is proportional to the concentration of nitrite and obeys Beer's law in the range 5 to 180 µg/L with 1 cm path at 520 nm.

Interference

Free chlorine or nitrogen trichloride that normally coexists with nitrite produce a false colour. This can be minimised by addition of naphthylamine hydrochloride. The following ions interfere because of precipitation under test condition and should be absent : Sb^{3+},Au^{3+},Bi^{3+},Fe^{3+}, Pb^{2+},Hg^{2+},Ag^{+}, $PtCl_6^{2-}$, VO_3^{2-} .

Reagents:

i) EDTA : Dissolve 500 mg EDTA sodium salt in distilled water and dilute to 100 mL.

ii) Sulfanilic acid : Dissolve 600 mg in 70 mL hot water. Cool and add 20 mL conc HCl and dilute to 100 mL.

iii) 1-Naphthylamine hydrochloride : Dissolve 600 mg

1-Naphthylamine hydrochloride in 100 mL distilled water containing 1 mL conc HCL , and store at low temperature. Discard when it decolourizes.

iv) Sodium acetate buffer, 2M: Dissolve 16.4 g sodium acetate and dilute to 100 mL.

v) Stock nitrite solution : Dissolve 1.232 g sodium nitrite and dilute to 1000 mL; 1 mL = 250µg.

Standardization of stock solution : Take 50 mL 0.05 N $KMnO_4$, add 5 mL conc H_2SO_4 and 50 mL stock nitrite solution well below surface by pipet. Warm to 70-80°C, decolourize $KMnO_4$ using 0.05 N sodium oxalate. Calculate NO_2^- by the equation:

$$A = \frac{(B \times C) - (D \times E) \times 7}{F}$$

where,

A = mg NO_2^--N/mL in stock $NaNO_2$ solution,

B = total mL standard $K\,MnO_4$ used,

C = normality of standard $K\,MnO_4$

D = total mL standard reductant added,

E = normality of standard reductant, and

F = mL stock $NaNO_2$ solution taken for titration

Each 1.00 mL 0.05 N $K\,MnO_4$ consumed by the $NaNO_2$ solution, corresponds to 350 µg NO_2 - N.

vi) Standard nitrite solution : Dilute appropriate aliquot of stock solution to 1000 mL so as to get 1 mL =0.5 µgN in the solution.

Procedure

i) Take 50 mL of sample and neutralize to pH 7.0.

ii) Add 1 mL of EDTA followed by 1 mL of sulfanilic acid and mix well.

iii) After 2-3 min add 1 mL 1-naphthylamine hydrochloride followed by 1 mL sodium accetate.

iv) Prepare blank in the same way by substituting water for the sample.

v) Measure colour after 10 min at 520nm and 1 cm cell path.

vi) Prepare calibration curve using suitable quantity of standard nitrite for reference.

vii) Read concentration from the calibration curve.

Reporting

Units......................mg/L.

Form(s)...................Nitrogen,nitrite(NO_2-N).

Significant figures........Less than 1.0 mg/L,nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

3.2.10.4 Nitrogen,organic

Principle

In the presence of sulfuric acid, potassium sulfate and mercuric sulfate catalyst, organically bound nitrogen gets converted into ammonium sulfate. During sample digestion, a mercury ammonium complex is formed and then decomposed by sodium thiosulfate. After decomposition the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia is determined colorimetrically or by titration with a standard mineral acid.

Interference

Nitrate in excess of 10 mg/L can oxidize a portion of the ammonia released from the digested organic nitrogen producing N_2O and resulting in a negative interference when sufficient organic matter in a low state of oxidation is present, nitrate can be reduced to ammonia resulting in a positive interference.

Reagents

i) Digestion reagent : Dissolve 134 g K_2SO_4 in 650 mL distilled water and 200 mL conc H_2SO_4. Add with stirring a solution prepared by dissolving 2 g HgO in 25 mL 6 N H_2SO_4. Dilute to 1000 mL and store at a temperature above 14°C to prevent crystallization.

ii) Phenolphthalein indicator : Dissolve 5g in 500 mL 95% ethyl alcohol. Add 500 mL distilled water. Add dropwise 0.02N NaOH till faint pink colour appears.

iii) Sodium hydroxide - Sodium thiosulfate reagent: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3$ and dilute to 1000 mL.

iv) Mixed indicator : Dissolve 200 mg methyl red in 100 mL 95% ethyl alcohol, 100 mg methylene blue in 500 mL 95% ethyl alcohol. Mix the two solutions.

v) Indicating boric acid: Dissolve 20g H_3BO_3 in distitilled water, add 10 mL mixed indicator and dilute to 1000 mL.

vi) Standard sulfuric acid : Prepare 0.1 N H_2SO_4 by diluting 3.0 mL conc H_2SO_4 to 1000 mL. Standardize it against standard Na_2CO_3,0.1N. Dilute appropriate volume of H_2SO_4(appro. 0.1 N) to 1000 mL to obtain standard 0.02 N H_2SO_4;1 mL=0.28 mgN.

Procedure

i) Take a known volume of well mixed sample in kjeldahl flask. If necessary, dilute sample to 300 mL.

ii) Add 50 mL digestion reagent. (In case suspended solids concentration is high, add large quantities of reagent to keep salt to acid ratio 0.8) and a few glass beeds and, after mixing, heat under a hood. boil briskly until the volume is greatly reduced (to about 25 to 50 mL) and capious white fumes are observed. Then continue to digest for an additional 30 min. As digestion continues, coloured or turbid samples will turn clear or straw coloured. After digestion, let flask and contents cool, dilute to 300 mL with water and mix. Tilt flask and carefully add 50 mL hydroxide-thiosulfate reagent to form a alkaline layar at flask bottom.

iii) Distill and collect 200 mL distillate below surface of 50 mL absorbent solution. Use plain boric acid solution when ammonia is to be determined by nesslerization and use indicating boric acid for a titrimetric method. Extend the tip of the condenser well below level of absorbent solution.

iv) When distillation is complete remove the flask containing distillate first and then put of heat to avoid back suction.

v) Determine the concentration of ammonia by nesslerization as directed in ammonia estimation. Titrate the distillate with N/50 sulfuric acid till the indicator turns a pale lavender colour.

vi) Carry a reagent blank through all the steps and apply necessary corrections.

Calculation

$$\text{Organic nitrogen, mg/L} = \frac{(A - B) \times 280}{\text{Volume of sample, mL}}$$

where,

A = Volume of 0.02N sulfuric acid required for sample mL, and

B = Volume of 0.02N sulfuric acid required for blank, mL.

Reporting

Units...................mg/L.

Form(s).................Nitrogen (N), Organic .

Significant figures......Less than 1.0 mg/L, nearest 0.1 mg/L; 1.0 mg/L and above, two significant figures.

3.2.11 Silica

Silica normally exists as an oxide (SiO_2 as in sand) or as a silicate (SiO_2^{2-} and SiO_3^{2-}). Silicon, the worlds's second most abundant element, is present in most waters and is considered one of the basic nutrients in water essential to the growth of certain phytoplankton and zooplankton species. Because of its wide prevalence in nature, it is doubtful if silica can be considered a limiting factor among the nutrient materials in water bodies. However, many researchers measure silica, in addition to nitrogen and phosphorous, to obtain a more complete picture of nutrient conditions in water. It has no known toxic effects and is used to form protective inner coatings on pipes to inhibit corrosion.

The silica content of natural water most commonly is in the 1 to 30 mg/L range, although concentrations as high as 100 mg/L are not unusual and concentrations exceeding 1000 mg/L are found in some brackish waters and brines.

Principle

Ammonium molybdate at a pH approximately 1.2 reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid but not the molydosilicic acid. Even if phosphate is known to be absent, the addition of oxalic acid is highly desirable and is a mandatony step. The intensity of the yellow colour is proportional to the concentration of 'molybdate-reactive' silica. The yellow molybdo silicic acid is reduced to heteropoly blue by amino naphthol sulfuric acid which increases sensitivity of the method.

Interference

Phosphate, tannin, large amounts of iron, colour, turbidity, sulfide are potential sources of interferences. Interferences caused by phosphate and tannin can be eliminated by addition of oxalic acid. The interference due to colour and turbidity can be compensated by using an appropriate blank.

Reagents

i) Hydrochloric acid, HCL, 1 + 1.

ii) Ammonium molybdate reagent : Dissolve 10 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in distilled water and dilute to 100 mL. Adjust pH to 7-8 and store in a polyethylene bottle.

iii) Oxalic acid solution : Dissolve 7.5 g oxalic acid, $H_2C_2O_4.H_2O$, in distilled water and dilute to 100 mL.

iv) Stock silica solution : Dissolve 4.73 g sodium metasilicate nonahydrate, $Na_2SiO_3.9H_2O$, in distilled water and dilute to 1000 mL. Analyze 100 mL portion by gravimetrically and dilute according to have 1000 mg/L SiO_2.

v) Standard silica solution : Dilute 10.00 mL stock solution to 1000 mL with distilled water; 1.00 mL = 10 µg SiO_2. Store in plastic bottle.

vi) Reducing agent : Dissolve 500 mg 1-amino-2-naphthol-4-sulphonic acid and 1 g Na_2SO_3 in 50 mL distilled water. Add this to a solution of 30 g $NaHSO_3$ in 150 mL distilled water. Filter through whatman paper No. 42 and store in a plastic bottle.

Procedure

i) Take 50 mL sample and add 1.0 mL 1+1 HCL and 2.0 mL ammonium molybdate reagent. Mix by inverting at least six times and let stand for 5 to 10 min.

ii) Add 2.0 mL oxalic acid solution and mix thoroughly, wait at least 2 min but not more than 15 min, add 2.0 mL reducing agent, and mix thoroughly. A blue colour will develop if silica is present.

iii) Allow five minutes for full colour development and measure blue colour photometrically at 690 nm using 1 cm light path.

iv) In case of clear samples prepare blank substituting sample by water and processing through all above steps.

v) Prepare a standard curve using standard silica solution covering 0.0 to 240 µg SiO_2.

vi) Calculate the concentration from standard curve.

Calculation

$$SiO_2, \text{ mg/L} = \frac{\mu g\ SiO_2 (\text{in 55 mL final volume})}{\text{ml sample}}$$

Reporting

Units.........................mg/L.

Form(s).................. Silica(SiO_2), reactive.

Significant figures....0.04 to 0.99 mg/L, two decimal places; 1.0 to 2.0 mg/L, two significant figures.

3.3 Organic Parameters

3.3.1 Biochemical oxygen demand

Biochemical oxygen Demand (BOD) is an empirical measurement of the oxygen requirement of muncipal and industrial waste waters and sewage. The test measures the oxygen required for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous ions. It also may measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by inhibitor. The test is of greatest value after patterns of oxygen uptake for a specific effluent and receiving water have been established.

The method consists of placing a sample in a full, airtight bottle and incubating the bottle for the standard five day period at 20+1°C. Dissolved oxygen (DO) is measured initially and after incubation. The BOD is computed from the difference between initial and final DO.

Most waste waters contains more oxygen demanding materials than the amount of DO available in air saturated water. Therefore, it is necessary to dilute the sample before incubation to bring the oxygen demand and supply into appropriate balance. Because bacterial growth requires nutrients such as nitrogen, phosphorous, and trace metals, these are added to the dilution water, which is buffered to ensure that the pH of the incubated sample remains in a range suitable for bacterial growth. Complete stabilization of the sample may require a period of incubation too long for practical purposes, therefore, five-day has been accepted as the standard incubation period.

Interference

Since the DO estimation is the basis of BOD test, sources of interference in BOD test are the same as in the DO test. In addition, lack of nutrients in dilution water, lack of an acclimated seed organisms, and presence of heavy metals or other toxic materials such as residual chlorine are other sources of interference in this test.

Reagents

i) Phosphate buffer: Dissolve 8.5 g KH_2PO_4, 21.75 K_2HPO_4, 33.4 g $Na_2HPO_4.7H_2O$ and 1.7 g NH_4Cl in distilled water and dilute to 1 L. Adjust pH to 7.2.

ii) Magnesium sulfate solution : Dissolve 22.5g $MgSO_4.7H_2O$ in distilled water and dilute to 1 L.

iii) Calcium chloride solution : Dissolve 27.5 g anhydrous $CaCl_2$ in distilled water and dilute to 1 L.

iv) Ferric chloride solution : Dissolve 0.25 g $FeCl_3.6H_2O$ in distilled water and dilute to 1 L.

v) Manganous sulfates solution : Dissolve 480 g $MnSO_4.4H_2O$ or 400 of $MnSO_4.2H_2O$, or 364 g $MnSO_4.\ H_2O$ in distilled water, filter and dilute to 1 L. The MnSO solution should not give a colour with starch when added to an acidified potassium iodide solution.

vi) Alkali-iodide-azide reagent : Dissolve 500 g NaOH (or 700 g KOH) and 135 g NaI (or 150 g KI) in distilled water and dilute to 1 L. Add 10 g NaN_3 dissolved in 40 mL distilled water.

Procedure

i) Place desired volume of distilled water in a suitable bottle and add 1 mL each of phosphate buffer, magnesium sulfate, calcium chloride and ferric chloride solutions/I of distilled water. Add 2 mL settled sewage and aerate.

ii) Neutralize sample to pH 6.5 to 7.5 if it is highly alkaline or acidic.

iii) The sample should be free from residual chlorine. If it contains residual chlorine remove it by using sodium sulfite solution as follows :

Take 100 mL of the sample and acidify with addition of 10 mL 1+1 acetic acid. Add about 10 mL potassium iodide solution (10 g/100 mL) and titrate with sodium sufite solution, 0.025 N, using starch indicator. Calculate the volume of sodium sulfite required per mL of the sample and add accordingly to the sample to be tested for BOD.

iv) Samples supersaturated with DO i.e., samples containing more than 9 mg/L due to either algal growth or some other reason, reduce the DO content by aerating and agitating the sample.

v) Make several dilutions of the prepared samples so as to obtain about 50% depletion of DO in dilution water but not less than 2 mg and the residual oxygen after 5 days of incubation should not be less than 1 mg/L. Prepare dilutions as follows:

0.1 to 1%	... Strong industrial wastes
1 to 5%	... Raw or settled waste water
5 to 25%	... Treated effluents
25 to 100 %	... River waters

vi) Siphon the silution prepared as above in 4 labelled BOD bettles and stopper immediately.

vii) Keep 1 bottle for determination of the initial DO and incubate 3 bottles at 20°C for 5 days.

viii) Prepare a blank in duplicate by siphoning plain dilution water (without seed) to measure the O_2 consumption in dilution water.

ix) Fix the bottles kept for immediate DO determination and blank by adding 1 mL $MNSO_4$ followed by 1 mL alkali iodide-azide reagent.

x) Determine DO in the sample and in the blank on initial day and after 5 days.

Calculation

Calculate BOD of the sample as follows:

Let D_o = DO in the sample bottle on 0^{th} day

D_1 = DO in the sample bottle on 5^{th} day

C_o = DO in the blank bottle on 0^{th} day

C_1 = DO in the blank bottle on 5^{th} day

C_o-C_1 = DO depletion in the dilution water alone

D_o-D_1 = DO depletion in the sample + dilution water

$(D_o-D_1) - (C_o-C_1)$ = DO depletion due to microbes

BOD, mg/L = $(D_o-D_1) - (C_o-C_1)$ mg x decimal fraction of sample used.

Reporting

Units.................. mg/L.

Form(s)................ Oxygen (O_2), biochemical.

Significant figures.... One decimal throughout range.

3.3.2 Chemical Oxygen Demand

The Chemical Oxygen Demand (COD) test is used to estimate the amount of organic matter in waste water. It is a measurement of the oxygen equivalent of the materials present in the waste water that are subject to oxidation by a strong chemical oxident, in this case dichromate. When waste water contains only readily available organic bacterial food and not toxic matter, the COD test results provide a good estimate of BOD values.

The dichromate reflux method test is performed by boiling a measured sample with a measured excess quantity of a potassium dichromate-acid standard solution. Dichromate is consumed in the oxidation of the organic matter, and the COD can be determined either colorimetrically, by measuring the increase in green colour of the reduced chromium (Cr^{3+}) or the decrease in yellow colour of the remaining dichromate.

Principle

Most types of organic matter gets oxidized completely by potassium dichromate in the presence of sulfuric acid to produce carbon dioxide and water. The excess potassium dichromate remaining after the reaction is titrated with ferrous ammonium sulfate to determine the amount of potassium dichromate consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent.

Interference

Fatty acids, straight chain aliphatic compounds, chlorides, nitrites and iron are the main source of interference.

The interference caused by chlorides can be eliminated by the addition of mercuric sulfate to the sample prior to addition of other reagents. About 0.4 g of mercuric sulfate is adequate to complex 40 mg chloride ions in the form of poorly ionized mercuric chloride.

Addition of silver sulfate (Ag_2SO_4) to conc sulfuric acid (1 gm silver sulfate/75 mL acid) as a catalyst stimulates the oxidation of straight chain aliphatic and aromatic compounds.

Nitrite exerts a COD of 1.1 mg oxygen per mg nitrite-nitrogen. Sulfamic acid in the amount 10 mg for each mg nitrite-nitrogen may be added to potassium dichromate solution to avoid interference caused by nitrite.

Reduced inorganic species such as ferrous iron, sulfide, manganous manganese, etc. are oxidized quantitatively under the test conditions.

Reagents

i) Standard potassium dichromate solution, 0.0417 M:Dissolve 12.25 g $K_2Cr_2O_7$, dried at 103°C for 2 h, in distilled water and dilute to 1 L.

ii) Sulfuric acid reagent : Add Ag_2SO_4 crystals to conc H_2SO_4 at the rate of 5.5 g Ag_2SO_4/Kg H_2SO_4. Let stand 1 to 2 d to disslove Ag_2SO_4.

iii) Ferroin indicator solution : Dissolve 1.485 g 1, 10-Phenanthroline monohydrate and 695 mg $FeSO_4.7H_2O$ in distilled water and dilute to 100 mL.

iv) Standard ferrous amonium sulfate solution, approximately 0.25 M; Dissolve 98 g Fe $(NH_4)_2(SO_4)_2.6H_2o$ in distilled water. Add 20 mL conc H_2SO_4 , cool, and dilute to 1000 mL. Standardize this solution daily against standard $K_2Cr_2O_7$ solution as follows:

Dilute 10.0 mL standard $K_2Cr_2O_7$ to about 100 mL. Add 30 mL conc H_2SO_4 and cool. Titrate with ferrous ammonium sulfate solution using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator.

Molarity of ferrous ammonium sulfate =

$$\frac{\text{Volume of 0.0417 M } K_2Cr_2O_7 \text{ solution titrated, mL} \times 0.25}{\text{Volume of ferrous ammonium sulfate used in titration, mL}}$$

v) Mercuric sulfate, $HgSO_4$, crystals or powder.

Procedure

i) Take 50 mL or fraction diluted to 100 mL with distilled water in a round bottom flask.

ii) Add 1 g mercuric sulfate, several glass beeds, and very slowly add 5 mL sulfuric acid reagent, with mixing to dissolve mercuric sulfate. Cool while mixing to avoid possible loss of volatile materials.

iii) Add 25.0 mL 0.0417 M potassium dichromate solution and mix. Attach flask to condenser and turn on cooling water. Add remaining sulfuric acid reagent (70 mL) through open end of condenser. Continue swirling and mixing while adding the sulfuric acid reagent.

iv) Cover open end of condenser with a small beaker to prevent foreign material from entering refluxing mixture and reflux for 2 h. Cool and wash down condenser with distilled water. Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water .

v) Titrate excess potassium dichromate with ferrous ammonium sulfate solution, 0.1 N, using ferroin indicator. Sharp colour change from blue green to wine red indicates end point of the titration.

vi) Reflux blank in the same manner using distilled water insted of sample.

Calculation

$$\text{COD, mg/L} = \frac{(A - B)M \times 8000}{\text{Volume of sample, mL}}$$

where,

A = Volume of ferrous ammonium sulfate used for blank, mL.

B = Volume of ferrous ammonium sulfate used for sample, mL, and

M = Molarity of ferrous ammonium sulfate.

Reporting

Units................. mg/L.

Form(s)............... Oxygen (O_2), chemical.

Significant figures... One decimal throughout range.

3.3.3 Total Organic Carbon

The content of organic carbon in water is one of the most important parameters of the quality of water, and is the most reliable characteristic of the total content of organic substance. The sum total of organic substances, which is represented by the concentration of organic carbon above and below the source of pollution, may serve as quite a useful pollution index of a body of water. This value is used when establishing the pollution zone and the zone of influence of drainage waters.

The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. Some of these carbon compounds can be oxidized further by biological or chemical processes, and the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) may be used to characterize these fractions. The presence of organic carbond that does not respond to either the BOD or COD test makes them unsuitable for the measurement of total organic carbon. Total organic carbon (TOC) is a more convenient and direct expression of total organic content than either BOD or COD, but does not provide the same kind of information.

Organic carbon, depending on the purpose of research is determined in a filtered or an unfiltered sample of water. In the former case, the determined carbon content is called the concentration of the dissolved organic carbond content. The sample used for the determination of the dissolved organic carbon is filtered through a 0.45 m membrane filter and is preserved with sulfuric acid or with mercury (II) chloride. The sample used for total organic carbond determination is not filtered, and the sample is kept cold at 3 to 4°C untill it is analysed.

Principle

The sample is homogenized and diluted as necessary and a microportion is injected into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide. The water is vaporized and the organic carbon is oxidized to CO_2 and H_2O. the CO_2 from oxidation of organic and inorganic carbon is transported in the carrier gas streams and is measured by means of a nondispersive infrared analyzer.

Because total carbon is measured, inorganic carbon(IC) must be measured separately and total organic carbon (TOC) obtained by difference.

Measure IC by injecting the sample into a separate reaction chamber packed with phosphoric acid-coated quartz beads. Under the acidic conditions, all IC is converted to CO_2, which is measured. Under these conditions organic carbon is not oxidized and only IC is measured.

Interference

Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles also can be lost during sample blending, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection.

Reagent

i) Reagent water: Prepare blanks and standard solutions from carbon-free water preferably used carbon-filtered, redistilled water.

ii) Phosphoric acid, H_3PO_4, Conc. Alternatively use sulfuric acid, H_2SO_4.

iii) Organic carbon stock solution: Dissolve 2.1254g anhydrous potassium biphthalate, $C_8H_5KO_4$, in carbon free water and dilute to 1000 mL; 1.00 mL = 1.00 mg carbon. Alternatively, use any other organic-carbon-containing compound of adequate purity, stability and water solubility. Preserve by acidifying with H_3PO_4 or H_2SO_4 to pH $<$2.

iv) Inorganic carbon stock solution : Dissolve 4.4122g anhydrous sodium carbonate, Na_2CO_3, in water, add 3.4 g anhydrous sodium bicarbonate, NaHCO , and dilute to 100 mL; 1.00 mL = 1.00 g carbon. Do not acidify.

v) Carrier gas: Purified oxygen or air, CO_2-free and containing less than 1 ppm hydrocarbon (asmethane).

vi) Purging gas: Any gas free of CO_2 and hydrocarbons.

Procedure

i) Instrument operation : Follow manufacturer's instructions for total organic carbon analyzer assembly, testing, calibration, and operation. Adjust to optimum cumbustion temperature (900°C) before using instrument, monitor temperature to insure stability.

ii) Sample treatment : If a sample contains gross solids or insoluble matter, homogenize untill satisfactory replication is obtained. Analyze a homogenizing blank consisting of reagent water carried through the homogenizing treatment.

If inorganic carbon must be removed before analysis, transfer a representative portion of 10 to 15 mL to a 30-mL beaker, add conc H_3PO_4 to reduce pH to 2 or less, and purge with gas for 10 min. Do not use plastic tubing. Inorganic carbon also may be removed by stirring the acidified sample in the beaker while directing a stream of purgified gas into the beaker. Because volatile organic carbon will be lost during purging of the acidified solution, report organic carbon as total nonpurgeable organic carbon.

If the available instrument provides for a separate determination of inorganic carbon and total carbon, omit decarbonation and proceed according to the manufacturer's directions to determine TOC by difference between TC amd IC.

iii) Sample injection: Withdraw a portion of prepared sample using a syninge fitted with a blunt-tipped needle. Select sample volume according to manufacturer's direction. Stir samples containing particulates with a magnetic stirrer. Select needle size consistent with sample particulate size. Inject samples and standards into analyzer according to manufacturer's direction, and record response. Repeat injection until consecutive peaks are obtained that are reproducible to within ± 10%.

iv) Preparation of standard curve: Prepare standard organic and inorganic carbond series by diluting stock solutions to cover the expected range in samples. Inject and record peak height of these standards and a dilution water blank. Plot carbon concentration in mg/L against corrected peak height in millimeters on rectangular coordinate paper. This is unnecessary for instruments provided with digital readout of concentration.

Calculation

i) Calculate corrected peak height of standards and samples by subtracting the reagent-water blank peak height from the standard and sample peak heights.

ii) Prepare a standard curve of corrected peak height vs. TOC concentration.

iii) Subtract the procedural blank from each sample peak height and compare to the standard curve to determine carbon content.

iv) Apply the appropriate dilution factor when necessary.

v) Subtract the inorganic carbon from the total carbon when TOC is determined by difference.

Reporting

Units.................mg/L.
Form(s)..............Carbon.
Significant figures... Two or three.

3.3.4 Oil and Grease

In the determination of oil and grease, an absolute quantity of a specific substance is not measured. Rather, groups of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in trichlorotrifluoroethane. Oil and grease is any material recovered as a substance soluble in trichlorotrifluoroethane. It includes other materials extracted by the solvent from an acidified sample (such as sulfur compounds certain organic dyes, and chlorophyll) and not volatilized during the test.

Oil may be present in anatural waters from the decomposition of plankton and/or higher forms of aquatic life. Most of oil and grase are insoluble in water but can be emulsified or saponified by alkalis, detergents and other chemicals. Some lighter petroleum fractions evidence a slight water solubility and may form a slick on the water surface oil and grease in water generally indicates pollution from industrial wastes. Certain constituents measured by the oil and grease analysis may influence waste water treatment system. If present in excessive amounts, they may interfere with aerobic and anaerobic biological processes and lead to decreased waste water treatment efficiency. When discharged in waste water or treated effluents, they may cause surface films and shoreline deposits leading to environmental degradation.

Principle

Dissolved or emulsified oil and grease is extracted from water by intimate contact with trichlorotrifluoroethane. Some extractables, especially unsaturated fats and fatty acids, oxidise readily, hence special precautions regarding temperature and solvent vapor displacement are included to minimize this effect.

Interference

Trichlorotrifluoroethane has the ability to dissolve not only oil and grease but also other organic substances. Solvent removal results in the loss of short chain hydrocarbons and simple aromatics by volatilization. In addition, heavier residuals of petroleum may contain a significant portion of materials that are not extractable with the solvent.

Reagents

i) Hydrochloric acid, HCl, 1 + 1.

ii) Trichlorotrifluoroethane (1, 1, 2-trichloro-1,2,2-trifluoroethane boiling point 47°C.

Procedure

i) Collect about 1L of sample in a wide mouth glass bottle and mark sample level in bottle for later determination of sample volume.

ii) Acidify the sample to pH 2 or lower (generally, 5 mL HCl is sufficient) and transfer to a separatory funnel.

iii) Rinse sample bottle with 30 mL trichlorotrifluoroethane and add solvent washings to separatory funnel. Stopper and shake vigorously for 2 min. However, if it is suspected that a stable emulsion will form, shake gently for 5 to 10 min.

iv) Remove the stopper and allow the funnel to stand undisturbed for 10 min. While the layers separates.

v) Drain solvent layer through a funnel containing solvent-moistened filter paper into a clean, tared distilling flask.

vi) Extract twice more with 30 mL solvent each. Combine extracts in distilling flask and wash filter paper with an additional 10 to 20 mL solvent.

vii) Distill solvent from distilling flask in a water bath at 70°C place flask on a water bath at 70°C for 15 min. and draw air through it with an applied vacuum for the final

1 min.

viii) Cool in a desicatorfor 30 min. and weigh.

Calculation

If the organic solvent is free of residue, the gain in weight of the tared distilling flask is mainly due to oil and grease.

$$\text{Oil and grease, mg/L} = \frac{(A - B) \times 1000}{\text{Volume of sample, mL}}$$

where,

A = Gain in weight of tared flask, mg and

B = Residue from solvent blank after evaporation

Reporting

Units................. mg/L.

Form(s)............... Oil and grease.

Significant figures... Two.

3.4 Metal

3.4.1 Determinationof sodium and potassium by flame photometry

Flame photometry is an elegant method of rapid analysis of sodium, potassium calcium, etc., and other alkalies and alkaline earth elements. These chemical elements provide a flame of gas with a characteristic colouring. 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 the concentration of the element.

Sodium and potassium are accurately determined by this way which no other method permits.

Sodium

Sodium ,the sixth most common element, is present in nearly all natural waterson. The levels may vary from less than 1 mg Na/L to more than 500 mg Na/L. Relatively high concentrations may be found in brines and hard water softened by the sodium exchange process. Ratio of sodium to total cations is important in agriculture and human pathology. Soil permeability can be harmed by a high sodium ratio. High pressure boilers require feed water with less than 3mg/L sodium to sustain efficient operation.

Potassium

Potassium ranks seventh among the elements in order of abundance, yet its concentration in most drinking waters seldom reaches 20 mg/L. However, occasional brines contain more than 100 mg/L potassium.

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.

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.

Interfernce 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.

Reagents

i) Stock sodium solution : Dissolve 2.542 g NaCl dried at 140°C and dilute to 1000 mL with deionised water; 1.00mL= 1.00 mg Na.

ii) Intermediate sodium solution : Dilute 10.00 stock sodium solution with deionized water to 100 mL; 1.00 mL=0.100mg Na. Use this intermediate solution to prepare calibration curve in sodium range of 1 to 10 mg/L.

iii) Standard sodium solution : Dilute 10.00 mL of intermediate sodium solution with water to 100 mL; 1.00 mL = 0.010mg Na. Use this solution to prepare calibration curve in sodium range of 0.1 to 1.0 mg/L.

iv) Standard lithium solution : Use either lithium chloride or lithium nitrate to prepare standard lithium solution containing 1.00 mgLi/1.00 mL.

v) Stock potassium solution : Dissolve 1.907 g of KCl dried at 110°C and dilute to 1000 mL with deionised water; 1 mL = 1.00 mg K.

vi) Intermediate potassium solution : Dilute 10.00mL stock potassium solution with water to 100 mL; 1.00 mL=0.100mg K. Use this solution to prepare calibration curve in potassium range of 1 to 10 mg/L.

vii) Standard potassium solution : Dilute 10.00 mL intermediate potassium solution with water to 100 mL; 1.00 ml = 0.010 mg K. Use this solution to prepare calibration curve in potassium range of 0.1 to 1.0 mg/L.

Procedure

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

ii) Start the electrical supply and switch on the air supply. Stabilize the air. This needle should be steady at the mark.

iii) Switch on the gas and maintain the gas fuel mixture so that the blue flame is seen through the viewing window.

iv) 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.

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

vi) Prepare a calibration curve from the standards.

vii) Determine concentration of sample from the calibration curve.

Calculation

Sodium or potassium mg/L = mg sodium or potassium/L in portion x D.

where,

$$D = \text{Dilution ratio}$$

$$= \frac{\text{mL sample} + \text{mL distilled water}}{\text{mL sample.}}$$

Reporting

Units.................mg/L.

Form(s)...............Sodium or potassium, dissolved.

Significant figures...Less than 10 mg/L,one decimal place; 10 mg/L and above, two significant figures.

3.4.2 Determination of Cadmium,Calcium,Chromium,Cobalt, Copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, silver, sodium, strontium, and zinc by atomic absorption spectrometry.

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 of water and effluents. Almost every known metallic element can be determined by means of this tool. In most cases, trace amount of an element can be identified in the presence of much higher concentration of other elements.

Two important reasons for the widespread use of atomic absorption spectrometric analysis are:

i) Sample preparation, in most instances, can be kept to a minimum for a great number of elements.

ii) Ease of instrument operation and sensitivity compete with most analytical methodology.

Cadmium

Cadmium is highly toxic when taken by mouth or inhaled and has been implicated in some cases of food poisoning. Minute quantities of cadmium are suspected of being responsible for adverse changes in arteries of human kidneys. A concentration of 200 micrograms per liter has been found lethal to certain fish. Recent work has shown, however; that traces of cadmium may be essential to proper diet. Cadmium can enter a water supply as the result of plating bath or other industrial discharges or through the deterioration of galranized plumbing.

Calcium

Calcium, the fifth most common element, is found in most natural water at levels ranging from zero to several hundred milligrams per liter, depending on the source and treatment of the water. Small concentrations of calcium carbonate combat corrosion of metal pipes by laying down a protective coating. Appreciable calcium salts, on the other hand, precipitate on heating to form harmful scale in boilers, pipes, and cooking utensils. Calcium contributes to the hardness properties of water and test results usually are reported as calcium hardness (mg/L equivalent calcium carbonate).

Chromium

Chromium may be present in water as the hexavalent or the trivalent form, although trivalent chromium rarely occurs in potable water. Hexavalent chromium enters a water supply through industrial wastes. From metal plating baths and from industrial cooling towers where chromate is used to inhibit metal corrosion. Chromium is an objectionable contaminant in public drinking water supplies due to its suspected carcinogenic effect. Chromium present in potable waters above a 3 μg/L level indicates the presence of industrial wastes. Concentrations greater than 50 μg/L are sufficient grounds for rejection of the water supply.

Cobalt

Seldom found in natural waters, cobalt often is present in industrial wastewaters as a corrosion product of stainless steel, nickel or cobalt alloys, and from metal plating baths. Cobalt is considered to be relatively nontoxic to man. The toxicity of cobalt to aquatic life indicates that tolerances vary widely and are influenced by species, pH, synergetic effects and other factors.

Copper

Copper may occur in natural water, wastewaters and industrial effluents as soluble copper salts or as precipitated copper compounds on suspended solids. Trace amounts of copper are necessary for normal body metabolism and its absence is known to cause nutritional anemia in children. Large oral doses of copper can cause emesis and may eventually result in liver damage. Though copper salts are often added to pounds to control aquatic plant life, large amounts have been shown to be toxic to fish. Copper generally is not considered a health hazard, but more than 1 mg/L copper can impart a bitter taste to the water. The average concentration of coper is potable waters is 0.03 mg/L and occasionally will range upto 0.6 mg/L in natural water from some areas.

Iron

Natural waters contain variable but minor amounts of iron despite its universal distribution and abundance. Iron in ground water is normally present in the ferrous (Fe^{++}) or soluble state which is easily oxidized to ferric (Fe^{+++}) or insoluble iron on exposure to air. Iron can enter a water system by leaching natural deposits, from iron-bearing industrial wastes, effluents from picking operations, or acidic mine drainage.

Iron in domestic water supply systems stains laundry and porcelain, causing more of a nuisance than a potential health hazard. Taste thresholds of iron in water are 0.1 mg/L ferrous iron and 0.2 mg/L ferric iron, giving a bither or astringent taste. Water used in industrial processes usually contain less than 0.2 mg/L total iron. Domestic water supplies containing more than 0.3 mg/L total iron should be rejected due to staining and taste considerations.

Lead

Lead seldom is found in ground water in more than trace quantities and averages about 10 µ g/L. Natural waters also contain very low levels of lead due to its tendency to be precipitated by a large number of substances. The level of lead in public water supplies usually is very low (less than 10 μg/L) unless storage tanks have been painted with a lead-base paint or lead piping or fixtures have been used in the delivery system.

Lead, a serious poison, tends to accumulate in the bone structure when ingested in levels exceeding the natural elimination rate of about 300 μg Pb/day. Accumulation of significant amounts of lead in the body may result in severe and permanent brain damage, conrulsions and death.

Lead in water normally indicates the intrusion of industrial, mine or smelter wastes or the decomposition of lead plumbing fixtures and pipes. The exact amount of lead which constitutes a lethal dose is not known but more than 50 μ g/L lead in drinking water is considered grounds for rejection of the supply.

Magnesium

Megnesium ranks eighth among the elements in order of abundance and is a common constituent of natural water. It contributes to the hardness properties of water and break down when heated forming scales in boilers. Concentrations greater than 125 mg/L also can have a cathartic and diuretic effect. Chemical softening, reverse osmosis, electrodialysis, or ion-exchange reduces the magnesium and associated hardness to acceptable levels. The level of magnesium may vary from zero to several hundreds milligrams per liter, depending on the source and treatment of the water.

Manganese

Manganese is present in ground waters as the divalent ion (Mn^{++}) due to lack of subsurface oxygen. Surface waters may contain combinations of manganese in various oxidation states as soluble complexes or as suspended particles.

The occurrence of manganese in public water supplies presents more of an economic problem than a potential health hazard. Manganese causes dark stains in laundry and on plumbing fixtures, tends to deposit in water lines, and imparts an objectionable task to beverages such as coffee and tea. Manganese in natural waters rarely exceeds 1 mg/L, but levels of 0.1 mg/L are sufficient to cause taste and staining problems. The maximum allowable manganese level in public water supplies 0.05 mg/L with the total iron plus manganese content not to exceed 0.3 mg/L.

Mercury

Mercury is not commonly found in natural waters and its presence indicates pollution by industrial wastes from metal processing, pharmaceutical or chemical manufacturing plants. Mercury also can enter the water system through agricultural pesticide, herbicide and fungicide residues, or through residual medicinal compounds. Organic phenyl and alkyl mercury residues (typically as phenyl mercuric acetate or methyl mercury) are the most commonly found mercury complexes in water and have identical toxicity properties to elemental mercury.

Prologed mercury ingestion can cause loss of muscle control, kidney damage, personality changes and permanent brain damage. Both inorganic and organically bound forms of mercury can be absorbed through the skin, causing burns and damage to internal membranes. Acute dosages in humans usually cause death within 10 days.

Nickel

Nickel, seldom found in natural waters, is often present in industrial wastwaters as a corrosion present is industrial wastewaters as a corrosion product of stainless steel and nickel alloys product of stainless steel and nickel alloys and from metal plating baths. Nickel is considered relatively nontoxic to man. The toxicity of nickel to aquatic life indicates that tolerances vary widely and are influenced by species, pH, synergetic effects and other factors. Nickel salts at concentrations between 0.5 to 1.0 mg/L have been shown to be injurious to a number of plant species.

Potassium

Potassium ranks seventh among the elements in order of abundance, yet its concentration in most drinking water seldom reaches 20 mg/L. However, occasional brines contain more than 100 mg/L potassium.

Silver

Silver can cause argyria, a permanent, blue-gray discoloration of the skin and eyes that imparts a ghostly appearance. Concentrations in the range of 0.4 to 1 mg/L have caused pathological changes in the kidneys, liver and spleen of rats. Toxic effects on fish in fresh water have been observed at concentration as low as 0.1 M g/L. Relatively small quantities of silver are bactericidal or bacterio static and find limited use for the disinfection of swimming pool and waters.

Sodium

Sodium, the sixth most common element, is present in nearly all natural waters. The levels may vary from less than 1 mg Na/L to more than 500 mg Na/L. Relatively high concentration may be found in brines and hard water softened by the sodium exchange process. Ratio of sodium to total cations is important in agriculture and human pathology. Soil permeability can be harmed by a high sodium ratio. High pressure boilers require feed water with less than 3 mg/L sodium to sustain efficient operation.

Strontium

A typical alkaline-earth element, strontium chemically resembles calcium and causes a positive error in gravimetric and titrimetric methods for the determination of calcium. Because it has a tendency to accumulate in bone, radioactive strontium 90, with a half-life of 28 years, presents a well-recognized peril to health. Naturally occurring strontium is not radioactive. For this reason, the determination of strontium in a water supply should be supplemented by a radiological measurement to exclude the posibility that the strontium content may originate from radioactive contamination.

Zinc

Zinc is essential to human metabolism and has been found necessary for proper body growth. High concentrations of zinc in water act as stomach irritants but the effects are temporary. Concentrations above 5 mg/L show no harmful physiological effects but can cause a bitter taste and/or an opalescene in alkaline drinking water.

Zinc concentration in most water supplies average about 1 mg/L but may range as high as 50 mg/L in some area. though zinc is commonly found in many natural waters, the deterioration of galvanized iron and leaching of brass can add substantial amounts. Industrial effluents may contribute large amounts of zinc, and high concentrations suggests the presence of lead and cadmium, common impurifies from the glavanizing process.

Principle

Atomic absorption spectrometry resembles emission flame photometry in that a sample is aspirated into a flame and atomized. The major difference is that in flame photometry the amount of light emitted is measured, whereas in atomic absorption spectrometry a light beam is directed through the flame, into a monochromator, and on to a detector that measures the amount of light absorbed by the atomized element in the flame. For many metals difficult to determine by flame emission, atomic absorption exhibits superior sensitivity. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used, ·this makes the method relatively free from spectral or radiation interferences. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample.

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 not 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 the determination of manganese.

Reagents

i) Air, cleaned and dried through a suitable filter to remove oil, water and other foreign substances. The source may be a compressor or commercially bottled gas.

ii) Acetylene, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689 KPa acetylene.

iii) Metal free water: Use metal free water for preparing all reagents and calibration standards and as dilution water.

Prepare metal free water by deioniging tap water.

iv) Calcium solution: Dissolve 630 mg calcium carbonate in 50 mL of 1 + 5 HCL. if necessary, heat and boil gently to obtain complete solution. Cool and dilute to 1000 mL with water.

v) Hydrochloride acid, conc.

vi) Lanthanum solution: Dissolve 58.65 g lanthanum oxide, La_2O_3, in 250 mL conc hydrochloric acid add acid slowly until the material is dissolved and dilute to 1000 mL with water.

vii) Hydrogen peroxide, 30%

viii) Nitric acid, conc.

ix) Standard metal solutions: Prepare a series of standard metal solutions in the optinum concentration range by appropriate dilution of the following stock metal solutions with water containing 1.5 mL conc HNO_3L. Use reagents of the highest purity. For hydrates, use fresh reagents.

Cadmium: Dissolve 1.000 g cadmium metal in a minimum volume of 1 + 1 HCL. Dilute to 1000 mL with water, 1.00 mL = 1.00 mg Cd.

Calcium: To 2.497 g $CaCO_3$ and 50 mL water and add drepwise a minimum volume of conc HCl (about 10 mL) to complete solution. Dilute to 1000 mL with water; 1.00 mL = 1.00 mg Ca.

Chromium: Dissolve 2.828 g anhydrous potassium dichromate $K_2Cr_2O_7$, in about 200 mL water, add 1.5 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 1.00 mg Cr.

Cobalt: Dissolve 1.407 g cobaltic oxide, CO_2O_3, in 20 mL hot conc HCl. Cool and dilute to 1000mL with water; 1.00 mL = 1.00 mg Co.

Copper: Dissolve 1.00 g copper metal in 15 mL of 1 + 1 HNO_3 and and dilute to 1000 mL with water; 1.00 mL = 1.00mg Cu.

Iron: Dissolve 1.00 g iron wire in 50 mL of 1 + 1 HNO_3 and dilute to 1000 mL with water ; 1.00 mL = 1.00 mg Fe.

Lead: Dissolve 1.59 g lead nitrate, $pb(NO_3)_2$, in about 200 mL water, add 1.5 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL= 1.00 mg Pb.

Magnesium : Dissolve 4.952 g magnesium sulfate, $MnSO_4$ in 200 mL water, add 1.5 mL conc HNO_3 and dilute to 1000 mL with water, 1.00 mL = 1.00 mg Mg.

Maganese: Dissolve 3.076 g manganous sulphate, $MnSO_4.H_2O$, in about 200 mL water, add 1.5 mL conc HNO_3, and dilute to 1000 mL with water 1.00 mL = 1.00 mg Mn.

Mercury: Dissolve 1.354 g mercuric chloride, Hg_2Cl_2, in about 700 mL water, add 1.5 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 1.00 mg Hg.

Nickel: Dissolve 1.273 nickel oxide, NiO, in a minimum volume of 10% (v/v) HCl and dilute to 1000 mL with water; 1.00 mL = 1.00 mg Ni.

Potassium: Dissolve 1.907 of potassium chloride, KCl, in water and make up to 1000 mL ; 1.00 mL = 1.00 mg K.

Silver: Dissolve 1.575 of silver nitrate, $AgNO_3$, in water, and add 1.5 mL conc HNO_3, and make upto 1000 mL, 1.00 mL = 1.00 mg Ag.

Sodium: Dissolve 2.543 g sodium chloride,NaCl,dried at 140°C in water and make up to 1000 mL ; 1.00 mL = 1.00 mg Na.

Strontium: Dissolve 2.45 g strontium nitrate, $Sr(NO_3)_2$, in 1000 mL of 1% (v/v) HNO_3; 1.00 mL = 1.00 mg Sr.

Zinc: Dissolve 1.00 g zinc metal in 20 mL 1+1 HCl and dilute to 1000 mL with water; 1.00 mL = 1.00 mg Zn.

Procedure

i) Instrument Operation

Install a hollow cathode lamp for the desired metal in the instrument and roughtly set the wavelength dial according to table 6. Set slit width according to manufacturer's suggested setting for the element being measured. Turn on instrument, apply to the hollow-cathode lamp the current suggested by the manufacturer, and let instrument warm up untill 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.

Table 6 : Atomic Absorption Concentration Ranges with Direct Aspiration Atomic Absorption

Element	Wave length nm	Flame Gases*	Detection Limit mg/L	Sensitivity mg/L	Optimum Conc range mg/L
Cd	228.8	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	285.2	A-Ac	0.0005	0.007	0.02-2
Mn	279.5	A-Ac	0.01	0.05	0.1-10
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

+ The mor sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.

When analysis are finished, extinguish flame by turning off first acetylene and then air.

ii) Standardization

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 Ca and Mg calibration, mix 100 mL of standard with 10 mL lanthanum solution, before aspirating. 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 is unnecessary. Plot calibration curves based on original concentration of standards before dilution with lanthanum calcium or hydrogen peroxide solution.

iii) Analysis of sample

Rinse nebulizer by aspirating water containing 1.5 mL conc 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 Fe or Mn, mix 100 mL with 25 mL Ca solution. When determining Cr, mix 1 mL H_2O_2 with each 100 mL sample before aspirating.

Calculation

Calculate concentration of each metal ion by referring to the appropriate calibration curve prepared according to the above procedure.

4.0 CONCLUSION

Agencies like water works, industrial organisation, water pollution control boards are required to analyse water/waste water samples. The present manual may be useful to field agencies who are engaged in water quality analysis work as an extension work. The results of analysis may be interpreted to suit a particular purpose of either surveillance of water quality, of effluent quality or to assess the performance of waste water treatment plant.

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3. American Public Health Association, American Water Works Association and Water Pollution Control Federation, 1985, Standard methods for the Examination of Water and Wastewater, 16th ed., Washington, D.C., American Public Health Association.

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9. U.S. Environmental Protection Agency, 1974, Methods for Chemical Analysis of Water and Wastes: Cincinnati, U.S. EPA Environmental Monitoring and Support Laboratory.

10. U.S. Environmental Protection Agency, 1978, Method for Organochlorine Pesticides in Industrial Effluents, National Environmental Research Centre, Cincinnati, Ohio.

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APPENDIX - I

INDIAN STANDARDS FOR DRINKING WATER*

Sl.No.	Characteristics	Desirable Limit
1.	Colour, Hazen units, Max	10
2.	Odour	Unobjectionable
3.	Taste	Agreeable
4.	Turbidity, NTU, Max	10
5.	Dissolved solids, mg/L, Max	500
6.	pH Value	6.5 to 8.5
7.	Total hardness (as $CaCO_3$),mg/L Max.	300
8.	Calcium (as Ca), mg/L, Max	75
9.	Magnesium (as Mg), Mg/L, Max	30
10.	Copper (as Cu), mg/L, Max	0.05
11.	Iron (as Fe), Mg/L, Max	0.3
12.	Manganese (as Mn), Mg/L, Max	0.1
13.	Chlorides(as Cl), mg/L, Max	250
14.	Sulphate (as SO_4), mg/L, Max	150
15.	Nitrate (as NO_3), mg/L, Max	45
16.	Fluoride (as F), mg/L,	0.6 to 1.2
17.	Phenolic compounds (as C_6H_5OH) mg/L, Max	0.001
18.	Mercury (as Hg), Mg/L, Max	0.001
19.	Cadmium (as Cd), mg/L, Max	0.01
20.	Selenium (as Se), mg/L, Max	0.01
21.	Arsenic (as As), mg/L, Max	0.05
22.	Cyanide (as CN), mg/L, Max	0.05
23.	Lead (as Pb), mg/L, Max	0.1
24.	zinc (as Zn), mg/L, Max	5
25.	Anionic detergents (as MBAS), mg/L, Max	0.2
26.	Chromium (as Cr^{6+}), mg/L, Max	0.05
27.	Polynuclear aromatic hydrocarbons (as PAH), µg/L, Max	-
28.	Mineral oil, mg/L, Max	0.01
29.	Residual, free chlorine, mg/L, Min	0.2

30.	**Pesticides**	**Absent**
31.	Radioactive materials:	
	a) Alpha emitters, μ c/mL, Max	10^{-8}
	b) Beta emitters, μ c/mL, Max	10^{-7}

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* IS : 10500 - 1983

APPENDIX - II

INDIAN STANDARDS FOR INLAND SURFACE WATER FOR VARIOUS USES*

<u>Classes of Water</u>

Class A : Inland Surface Waters for Use as Drinking Water Source Without Conventional Treatment but after Disinfection

Class B : Inland Surface Waters for Outdoor Bathing

Class C : Inland Surface Waters for Use as Drinking Water Source With Conventional Treatment Followed by Disinfection.

Class D : Inland Surface Waters Used for Fish Culture and Wild Life Propagation

Class E : Inland Surface Waters for Irrigation, Industrial Cooling or Control Waste Disposal.

Sl.No.	Characteristic		Tolerance Limit			
		Class A	Class B	Class C	Class D	Class E
1.	2.	3.	4.	5.	6.	7.
1.	pH Value	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5
2.	Dissolved Oxygen, mg/L, Min	6	5	4	4	-
3.	Biochemical Oxygen demand (5 days at 20°C), mg/L, Max	2	3	3	-	-
4.	Total Coliform Organism , MPN/100mL, Max.	50	500	5000	-	-
5.	Colour, Hazen Units, Max	10	300	300	-	-
6.	Odour	Unobjection-able.	-	-	-	-
7.	Taste	Tasteless	-	-	-	-
8.	Total dissolved solids, mg/L,Max	500	-	1500	-	2100
9.	Total hardness (as $CaCO_3$), mg/L,Max	300	-	-	-	-

1.	2.	3.	4.	5.	6.	7.
10.	Calcium hardness (as $CaCO_3$), mg/L, Max	200	-	-	-	-
11.	Magnesium hardness (as $CaCO_3$), mg/L, Max	100	-	-	-	-
12.	Copper (as Cu), mg/L, Max	1.5	-	1.5	-	-
13.	Iron (as Fe), mg/L, Max	0.3	-	0.5	-	-
14.	Manganese (as Mn), mg/L, Max	0.5	-	-	-	-
15.	Chlorides (as Cl), Mg/L, Max	250	-	600	-	600
16.	Sulphates (as SO_4), mg/L, Max	400	-	400	-	1000
17.	Nitrates as (NO_3), mg/L, Max	20	-	50	-	-
18.	Fluorides (as F), mg/L, Max	1.5	1.5	1.5	-	-
19.	Phenolic Compounds (as C_6H_5OH)mg/L,Max	0.002	0.005	0.005	-	-
20.	Mercury (as Hg), mg/L, Max	0.001	-	-	-	-
21.	Cadmium (as Cd), mg/L, Max	0.01	-	0.01	-	-
22.	Selenium (as Se), mg/L, Max	0.01	-	0.05	-	-
23.	Arsenic (as As), mg/L, Max	0.05	0.2	0.2	-	-
24.	Cyanide (as CN), mg/L, Max	0.05	0.05	0.05	-	-
25.	Lead (as Pb), mg/L, Max	0.1	-	0.1	-	-
26.	Zinc (as Zn), mg/L, Max	15	-	15	-	-
27.	Chromium (as Cr^{6+}), mg/L, Max	0.05	-	0.05	-	-
28.	Anionic detergents (as MBAS), mg/L, Max.	0.2	1	1	-	-
29.	Polynuclear armatic hydrocarbons, (as PAH).	0.2	-	-	-	-
30.	Mineral Oil, mg/L, Max	0.01	-	0.1	0.1	-

1.	2.	3.	4.	5.	6.	7
31.	Barium (as Ba), mg/L, Max	1	-	-	-	-
32.	Silver (as Ag), mg/L, Max	0.05	-	-	-	-
33.	Pesticides	Absent	-	Absent	-	-
34.	Alpha emitters, μC/ML, Max	10^{-9}	10^{-9}	10^{-9}	10^{-9}	10^{-9}
35.	Beta Emitters, μC/mL, Max	10^{-8}	10^{-8}	10^{-8}	10^{-8}	10^{-8}
36.	Free ammonia (as N), mg/L,Max	-	-	-	1.2	-
37.	Electrical conductance at25°C,mhos,max	-	-	-	1000×10^{-6}	2250×10^{-6}
38.	Free Carbondiovide (as CO_2), mg/L Max	-	-	-	6	-
39.	Sodium absorption ratio	-	-	-	-	26
40.	Boron (as B), mg/L, Max	-	-	-	-	2
41.	Percent Sodium, Max	-	-	-	-	60

APPENDIX - III

List of Indigeneous Equipment Available for Water Analysis.

1. pH Meter
2. Conductivity Meter
3. Dissolved Oxygen meter
4. Turbidimeter
5. Flame Photometer
6. Water Testing Kit
7. UV-VIS Spectrophotometer
8. Specific Ion Meter
9. Autoclave
10. Electronic Balance
11. BOD Incubator
12. Centrifuge
13. Deep Freezer
14. Muffle Furnace
15. Oven (hot air)
16. Hot Plate
17. Distillation Assembly
18. Magnetic Stirrer with Hot Plate
19. Filtration Pump (Vacuum)
20. Water Bath (Thermostatic)

APPENDIX - IV

List of Manufacturers of Water Analysis Equipment

1. M/S Systronics
   69/5A, Patwari Trust Compound
   Shivaji Marg, New Delhi-110015.

2. M/S Toshniwal Brothers Pvt. Ltd.
   3E/8, Jhandewalan Extension,
   New Delhi-110055

3. M/S Elico Pvt. Ltd.,
   2-E/6, Jhandewalan Extension,
   New Delhi - 110055.

4. M/S Control Dynamics Company,
   3, Int. Floore, Satya Mansion,
   Ranjit nagar Community Centre,
   New Delhi - 110008.

5. M/S Phillips India Ltd.,
   68, Shivaji marg
   New Delhi - 110015

6. M/S Century Instruments (P) Ltd.,
   S.C.O. 289, Sector 35-D,
   Chandigarh - 160036.

7. M/S Naina Electronics (P) Ltd.
   181/6, Industrial Area,
   Chandigarh - 160002.

8. M/S Narang Scientific Works Pvt. Ltd.,
   C-255, Mayapuri Industrial Area,
   Phase-II, New Delhi - 110064.

9. M/S A.J. Enterprises,
   3/224, Vishnupuri,
   Kanpur - 208002.

10. M/S Remi Equipments,
    14, Shah Industrial Estate,
    Veera Desai Road,
    Andheri (West),
    Bombay - 400058.