12.0

MATERIALS AND METHODS

12.0

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12.1 Water Quality Examination

The water quality examination comprises of physical, chemical, bacteriological and biological analysis.

Physical analysis determine the aesthetic quality and assess the performance of various treatment units.

Chemical analysis determine the amount of chemical substances which may affect the quality of water and be indicative of pollution and which reflect variations due to treatment - a requirement for control of water treatment processes.

Bacteriological examinations indicate the presence of bacterial characteristic of pollution and hence the safety of water for consumption.

Biological examinations will find application in providing information of causes of objectionable tastes and odours in water in or clogging of filters and dictating remedial measures.

12.2 Physico-chemical aspects

Although in the rural areas, great majority of water quality problems are related to bacteriological or other biological contamination, a significant number of very serious problems may occur as a result of chemical contamination of water sources. Such contamination may arise from certain industries, such as mining and smelting or from agricultural practices and mal-practices (e.g. the use and misuse of nitrates as fertilizers) or from natural sources (e.g. iron, fluoride).

In order to establish whether such problems exist, a selected number of Physico-chemical parameters may needed to be measured. However, particularly in the case of rural water supplies, it could be both very costly and physically impracticable to cover a large number of parameters.

12.3 Sampling

The collection of water samples may seem a relative simple task. However, to obtain representative water samples to preserve their integrity until they are analyzed in the laboratory, a series of steps, procedures and practices are required. A representative sample can easily be obtained from rivers and lakes which are relatively homogenous, where as many water-bodies have significant spatial and temporal variations and the collection of a representative sample becomes much more complex.

The objective of sampling is to collect a portion of material small enough in volume to be conveniently transported to and handled in the laboratory while still accurately

representing the material being sampled. This implies, first, that the relative portions of the concentrations of all pertinent components must be the same in the samples as in the material being sampled and second, that the sample must be handled in such a way that no significant changes in composition occure before the tests are performed. The analysis is generally intended to reveal the composition of the waters at the time or over the period of sampling. Consequently, errors are introduced if changes take place between taking of the sample and analysis being carried out. There is, infact, a strong likelihood that such changes will occur in most of the waters. The arrangement should be such that these are prevented or at least minimized.

The value o any laboratory analysis and test depends upon the method of sampling. Failure to observe proper precautions in securing a representative sample may result in an analysis which is of little use since it may unnecessarily condemn a good water supply or more frequently it may certify a bad water as satisfactory.

All samples of water should be properly labelled and should be accompanied by complete to accurate identifying and descriptive data. Data should include date and time of collection, type of source of the sample and temperature of water at the time of collection.

12.4 Selection of Sampling sites

The objectives of water quality monitoring system are ;

- To assess the impact of activities by man upon the quality of water and its suitability for required uses
- To determine the quality of water in its natural state which might be available to meet the future needs and
- To keep under observation the sources and path way of specified hazardous substances

The selection of sampling site is decided by the various uses of the water and by their location, relative magnitude and importance. The chances of accidental pollution is also an important factor and should be considered. The location of a river used down - stream of large urban or industrial area imposes greater risk and requires more supervision than similar uses located upstream.

The selection of the sites in the first place is decided on the basis of overall objective of the programme. Sampling points must be located to provide an accurate understanding of the existing quality of water. The sampling on extremely remote places should be avoided until of course, the special need arises and the facilities are adequate. Location of sampling sites can be helped considerably by taking the help of contour maps/ location maps for lakes and topographic maps for river.

The selection of actual sampling location in the waterbody shall depend upon the character of the waterbody. In a lake or a wide river main sampling sites should be selected at various corners. If the lake is stratified, three vertical samples at one site.

12.5 Collection of samples

Samples may be collected by using a water sampler or by using glass or polythene bottles. For a depth sample, a sampler is often necessary. For collection of a sample from the bottom, where water is shallow and a depth sampling is must, the sample can be collected by lowering a closed bottle to the bottom, opening and closing it there by hand and bringing at the surface. But in this case the surface sample must be collected first to avoid the disturbances caused by the loose sediment.

12.6 Type of Samples

12.6.1 Grab or catch samples

A sample collected at a particular time and place can represent only the composition of the source at that time and place. However, when a source is known to be fairly constant in composition over a considerable period of time or over substantial distances in all directions, the sample may be said to represent a larger time period or larger volume or both, than the specific point at which it was collected. In such circumstances, same source may be quite well represented by single grab sample. When a source is known to vary with time, grab samples collected at suitable intervals can be of great value in documenting the extent, frequency and duration of these variations. In case the composition of a source varies in space rather than in time, a set of samples collected from appropriate locations with less emphasis on timing may provide the most useful information.

12.6.2 Composite samples

The term composite refers to a mixture of grab samples collected at the same sampling point at different times. Sometimes the term time composite is used when it is necessary to distinguish this type of sample from other. Time composite samples are most useful for observing average concentrations as an alternative to the separate analysis of a large number of samples, followed by computation of average and total results. A composite sample of 24 Hr. period is considered standard for most determinations. Composite samples cannot be used for determinations of components or characteristics subject to significant and unavoidable changes or storage.

12.6.3 Integrated samples

Mixture of grab samples collected from different points simultaneously or as nearly as possible is called integrated sample. Such samples are useful for river

or stream that varies in composition across its width and depth. The need for integrated samples also may exist if combined treatment is proposed for several separate waste water streams. The preparation of integrated samples requires special equipment to collect samples from a known depth, without contamination by overlying water. Prior knowledge about volume, movement and composition of the various parameters of the water being sampled is also required.

Samples for physical and chemical examination should be collected in clean glass stoppered bottles made of neutral glass or polythene carboy with a minimum capacity of 2 litres. Stoppered glass bottles, technically known as 'Winchester Quarts' are suitable. Before collecting the sample, the bottle is well rinsed atleast three times with the water, filling in each time, about 1/3 full. Finally the bottle is filled, the stopper covered with a piece of cloth which is tied down tightly with string and sealed.

12.7 Preservation

Preservation of chemical samples, is difficult because almost all preservatives interfere with some of the tests. Immediate analysis is ideal. Storage at low temperature($4^{o}C$) is perhaps the best way to preserve most samples until the next day.

Use preservatives only when they are shown not to interfere with the analysis being made when they are used, add them to the sample bottle initially so that all sample portions are preserved as soon as collected.

No single method of preservation is entirely satisfactory, choose the preservative with due regard to the determination to be made. All methods of preservation may be inadequate when applied to suspended matter.

Methods of preservation are relatively limited and are intended generally to regard biological action, retard hydrolysis of chemical compounds and complexes and reduce volatility of constituents.

Preservation techniques are limited to.....

- A pH Control
- B Chemical addition
- C Refrigeration and
- D Freezing

Above techniques will be useful in the case of water quality monitoring looking to the local condition, water pollution survey, industrial waste and sewage analysis.

12.8 Sampling Frequency

The quality of water in various water bodies is rarely constant. Therefore, water samples should be collected at intervals so that no change in quality could pass unnoticed.

The larger the number of samples from which the mean is derived, the narrower will be the limit of the probable difference between observed and true values. However, the sampling schedule is a compromise between accuracy, funds and personnel for the work.

12.9 Number of samples

Number of samples and how often should samples be collected, are calculated by statistical considerations. The following frequencies of sampling may be adopted provisionally.

- Weekly samples for one year
- Daily samples for 7 days consecutively (4 times/year)
- Round the hour sampling 24 hours
- 4-hourly samples for 7 days and 4 times/year

The parameters may be limited during these sampling but should be pertinent to the source/ sampling station.

The analytical data collected as per the above procedure will help to lay proper emphasis on parameters of relative importance, their ranges, interference and frequencies of their occurrence.

12.10 Sample Containers

It is advantageous to measure the quantity of water in site by means of sensors which are lowered into position rather than by withdrawing samples. However, it is not always possible. Water samples are, therefore, collected in suitable containers. A sample container must satisfy the following requirements.

- it should easily be greed from contamination
- it should not change the relevant water characteristics
- it should have adequate capacity for storing the samples
- it should be resistant to impact and to internal pressure which is incresed by expansion of water or by release of dissolved gases at elevated temperature on storage

12.11 Sampling Procedure

The first thing to consider is the selection of the sampling point and great care and discretion are necessary in this selection in order that the sample shall represent as fairly as possible the source desired to be examined.

The suitability of the sampling point having been decided, the hand pump should be allowed to run for several minutes and the water from the sampling point allowed to run to waste for five minutes in order to free the sampling point from stagnant water before the sample is collected with care and expediency. The container should be completely filled with water and the stopper/ cap replaced. The container after labelling is replaced in the sampling box for immediate despatch to the laboratory for analysis.

12.12 Transportation of samples

Chemical analysis of collected samples, determine temperature, pH and dissolved gases (O_2, CO_2 etc.) in the field quickly after collecting of water samples, as the temperature changes quickly, pH may change significantly in a matter of minutes and dissolved gases may be lost.

Immediate analysis is ideal. However, where this is not feasible, water sample should be preserved as per recommended methods and transported to the laboratory at the earliest or within 72 hours for analysis purpose.

12.13 Sampling for Physical and Chemical Analysis

Samples should be collected in containers of pyrex glass or other inert material like polythene.

Sample bottles must be carefully cleaned before use. Glass bottles may be rinsed with a chromic acid cleaning mixture by adding one litre of concentrated sulphuric acid slowly with stirring to 35ml saturated sodium dichromate solution, or with an alkaline permanganate solution followed by an oxalic acid solution. After having been cleaned, bottles must be rinsed thoroughly with tap water and then with distilled water.

About 2.5 litres of the sample is required for analysis. Prior to filling, the sample bottle should be rinsed out two or three times with water to be collected. Care should be taken to obtain a sample that is truly representative of existing conditions and to handle it in such a way that it does not deteriorate or become contaminated before it reaches the laboratory.

The sample should reach the place of analysis as quickly as possible within 72 hours of collection. The time elapsed between collection and analysis should be recorded on the laboratory report.

Some determinations are likely to be affected by storage of samples. Walls of glass containers are likely to adsorb cations like aluminium, cadmium, chromium, copper, iron, lead, manganese, silver or zinc which are best collected in a separate bottle and acidified by concentrated hydrochloric or nitric acid to a pH approximately 3.5 to minimise precipitation and adsorption on the walls of the container.

Certain parameters like temperature, pH, dissolved gases like carbon dioxide, hydrogen sulphide, chlorine and oxygen may change significantly during transport. For this reason, determination of pH, carbon dioxide, ferrous iron, dissolved oxygen and chlorine should be carried out on the spot. Hydrogen sulphide can be preserved by fixing it with zinc acetate until the sample is ready for analysis.

Hot samples collected under pressure should be cooled while under pressure. Samples from wells should be collected only after the well has been pumped for a sufficient time to ensure that the sample will be representative of the ground water.

12.14 Colour

Preamble

Colour in water may result from the presence of natural metallic ions. (Iron and Manganese) humus and peat materials, plankton, weeds and Industrial wastes. Colour is removed to make a water suitable for general application.

The term "Colour" is used have to mean true colour, that is, the colour of water from which turbidity has been removed. The term "apparent colour" includes not only colour due to substances in solution, but also that due to suspended matter. To determine colour by currently accepted methods, turbidity must be removed before analysis. Filtration yields results that are reproducible.

Method

Visual comparison method : This method is applicable to nearly all samples of potable water.

Principle : Colour is determined by visual comparison of the sample with known concentration of coloured solution, comparison also may be made with special, properly calibrated glass colour disks. The platinum-cobalt method of necessarily colour is the standard method. Some way, colour disks is also convenient, where compare water colour with that of glass disks with comperator. Where glass comperator tubes filled with sample and colourless distilled water. Match sample colour with the colour of the tube of clear water plus the calibrated coloured Glass when viewed by looking toward a light; report colour in hazen unit from comparator.

12.15 Turbidity

The clarity of water is important to insure an acceptable use.

Turbidity in water is caused by suspended solids such as clay, silt, finely divided organic and inorganic matter, soluble coloured organic compounds, 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 line through the sample.

Nephelometric method :

Principle : This method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a Standard reference suspension under the same condition. The higher the intensity of scattered light, the higher the turbidity.

Interference : Turbidity can be determined for any water sample that is free of debris and rapidly settling coarse sediments, dirty glassware, the presence of air bubbles, and the effects of vibrations gives false results.

Apparatus : Nephelo- (turbido) - meter.

Reagents :

STOCK turbidity suspension.

- Solution - I: Dissolve 1.0 g hydrazine sulphate in distilled water and dilute to 100 ml in a volumetric flask.
- Solution - II: Dissolve 10 g hexamethylenetetramine in distilled water and dilute to 100ml in a Volumetic flask.
- In a 100 - ml volumetric flask, mix 5.0 ml Solution - I and 5.0 ml Solution - II. Let stand for 24 Hrs. dilute to mark and mix. The turbidity of this suspension is 400 NTU.

N.B. : Prepare solution and suspension monthly, make the STD. turbidity suspension from above stock solution.

Procedure :

- Operate Nephelometer by "Set zero" and required calibration.
- Shake sample thoroughly.
- Wait untill air bubbles disappear and pour sample in to turbidimeter tube.
- Read turbidity directly from instrumental scale and expressed in NTU.

12.16 Odour

Water is a neutral medium, always present on or at the receptors that perceive sensory response. Odour is recognised as a Quality factor affecting acceptability of drinking water and esthetics of recreationals waters.

Most organics and some inorganic chemicals contribute taste or odour. These chemicals may originate from municipal and industrial waste discharge, from natural source. Such as decomposition of vegetable matter, or from associated microbial activity, and from disinfectants or their products.

Many other sensations ascribed to the sense of taste actually are odours, eventhough the sensation is not noticed until the material is taken in to the mouth. Because some odourous material are detectable when present in only a few nanograms per liter, it is

usually impractical and often impossible to isolate and identify the odour-producing chemical. The ultimate odour-testing device is the human-nose.

Odour tests are performed to provide qualitative description.

12.17 pH

Principles : Measurement of pH is one of the most important and frequently used test in water chemistry. 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. pH is used in alkalinity and CO_2 measurements.

At a given temperature the intensity of the acidic or basic character of a solution is indicated by pH. Alkalinity and Acidity are the acid and base neutralizing capacities of water and usually expressed as $CaCO_3$ mg/l.

Buffer capacity is the amount of strong acid or base, usually expressed in moles per litre, needed to change the pH value of 1.0 litre sample by 1 unit.

pH defined as - log $[H^+]$

It is the "intensity" factor of acidity. Pure water is very slightly ionized i.e.

$$[H^+]\,[OH^+] = Kw$$
$$= 1.01 \times 10^{-14} \text{ at } 25^C$$

and $[H^+] = [OH^-]$

$$= 1.005 \times 10^{-7}$$

Where,

[H+] = activity of hydrogen ions mole/l

$[OH^-]$ = activity of hydroxyl ions moles/l

Kw = ion product of water

At 25°C, pH 7.0 is neutral, the activities of the hydrogen and hydroxyl ions are equal and each corresponds to the approximate activity of 10^{-7} moles/l.

Natural waters usually have pH values in the range of 4 to 9 and most are slightly basic, because of presence of HCO_3 - and CO_3 of the alkali and alkaline earth metals.

Electrometric method :

Principle : The basic principle of electrometric pH measurements is determination of activity of the hydrogen ions by potentiometric measurement.

Interference : The electrode is relatively free from interference from color, turbidity, colloidal matter, oxidants, reductants or high salinity. pH measurements are affected by temperature in two ways. Mechanical effect that are caused by change in the properties of the electrode and chemical effect caused by equilibrium change. Because chemical equilibrium effects pH, standard pH buffers have a specified pH at indicated temperature.

Always report temperature at which pH is measured.

Apparatus :

- pH Meter : For routine work, a pH meter accurate and reproducible to 0.1 pH unit with a range of 0 to 14 and equipped with a temperature compensation adjustment.

  NOTE : Generally, combination electrode in use, which incorporate the Glass and reference electrode in to a single probe.

  Procedure : Calibrate the electrode system against standard buffer solution of known pH.
- Sub-merge the electrode in sample, establish equilibrium between electrode and sample by stirring sample to insure homogenity.
- Record measurement of pH value from dial.

12.18 Solids

Solid mainly important in drinking water are suspended and dissolved. Waters with high TDS, generally are of inferior palatability and may induce an unfovourable physiological reaction in the transient consumer. Waters high in suspended solids may be esthetically unsatisfactory.

Definition: "Total Solids" is the termed applied to the material residue left in the vessel after evaporation of a sample and it's subsequent drying in an oven at a defined temperature. Total solids includes "T.S.S", the portion of T.S. retained by a filter and "TDS", the portion that passes through the filter.

NOTE :Fixed solids is a residue of total solids after heating to dryness for a specified time for specified temperature and the weight loss on ignition is called volatile solids.

Methodology : Total solids - 103°C to 105°C

Principle : A well-mixed sample is evaporated in a weighted dish and dried to constant weight in an oven at 103°C 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 Ca, Mg, Cl^-, and or SO4 may be hygroscopic and required prolonged drying, proper desiccation and rapid weighing.

Apparatus :

- Evaporating dishes or beakers.
- Porcelain dishes - 90mm dia.
- Drying oven - at 103°C to 105°C
- Muffle furnace - 500°C ± 50°C
- Analytical balance
- Dessicator
- Wide-bore pipets, cylinder etc.

Procedure :

- Clean and dry required beaker at 103°C to 105°C
- Cool in dessicator until needed
- Weigh immediately before use
- Add (put) a measured volume of well-mixed sample in pre-weighed beaker
- Evaporate to dryness in oven at 103°C to 105°C
- Cool in dessicator to balance temperature and weigh
- Repeat cycle of drying, cooling, desiccating and weighing until a constant weight is obtained.

Calculation :

$$\text{mg Total solids/l} = \frac{(A-B) \times 1000}{\text{Sample volume ml}}$$

Where,

A = Weight of dry residue + beaker (mg)

B = Weight of empty beaker (mg)

Total Dissolved Solids : (TDS)

Principle : A well-mixed sample is filtered through a standard filter paper (whatman-42) and filtrate is evaporated to dryness in a pre-weighted beaker and dried to constant weight at 180°C. The increase in weight represents the TDS. This procedure may be used for drying at other temperature.

Interference : Some as TS, sample high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the beaker may form a water-trapping crust.

Apparatus :

Addition to previous apparatus,

- Flasks
- Funnels
- Whatman - filter-paper-No-42

Procedure : same as T.S.

12.19 Hardness

Definition : In confirmity with current practice, Total hardness is defined as the sum of the Calcium and magnesium concentrations both expressed as calcium carbonate in mg/l. When hardness numerically is greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called "**Carbonate hardness**", the amount of hardness in excess of this is called "noncarbonate hardness". When the hardness numerically is equal to or less than the sum of carbonate and bicarbonate alkalinity, and hardness is carbonate hardness and noncarbonate hardness is

absent. The hardness may range from zero to hundreds of mg/l, depending on the source and treatment to which the water has been subjected.

Method :

EDTA titration method, measures the Calcium and magnesium ions and may be applied with appropriate modification to any kind of water. The procedure described affords a means of rapid analysis.

Principle:

EDTA and it's sodium salts form a chelated soluble complex when added to a solution of certain metal ions. If a small amount of a 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. If EDTA is added as a titrant, the calcium and magnesium will be complexed, and when all of the magnesium and calcium has been complexed, solution turns from wine red to blue, marking the end point of the titration.

Interference : Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA. Reduce this interference by adding certain inhibitors before titration.

Reagents:

- Buffer solution : Dissolve 1.179gm disodium salt of EDTA and 780 mg $MgSO_4$. $7H_2O$ in 50 ml distilled water. Add this solution to 16.9g NH_4Cl and 143 ml cone. NH_4OH with mixing and diluting to 250 ml with distilled water.Store in borosilicate glass containers.
- Eriochrome black-T indicators : (Sodium salt of 1 - (1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-Sulphonic acid. No-203 in the colour index. Dry powder form.0.5 gm crushed with 100gm inert salt.
- STD E.D.T.A. Titrant : (0.01 M) Weigh 3.723g di-sodium E.D.T.A salt, dissolve in distilled water dilute to 1 litre. Standardize against Std. Calcium Solution stored in borosilicate glass-bottle.
- STD Calcium solution : weight 1.000g anhydrous $CaCO_3$ in 500ml flask. Place a funnel in the flask neck and add 1 + 1 Hcl until $CaCO_3$ has dissolved. Add 200 ml distilled water and boil for a few minutes to expel CO_2, cool, add few drops of methyl red indicator and adjust to the intermediate orange colour by adding 3 N NH_4OH or 1 + 1 HCl as required, dilute to 1 lt. (1 ml = 1.0 mg $CaCO_3$.)
- NaOH (0.1 N)

  Procedure : Suitable sample portion is taken (i.e. 50 ml).

  Add 1 to 2 ml buffer solution to give pH 10 ± 0.1.

  Add appropriate amount of dry-powder indicator Eriochrome - black - T.

  Add STD EDTA Titrant slowly with continuous stirring, until blue end point comes.

Calculation : Hardness (EDTA) as mg $CaCO_3/l = \frac{A \times B \times 1000}{\text{ml. sample}}$

Where,

A = ml titration for sample and

B = mg $CaCO_3$ equivalent to 1.00ml E.D.T.A. titrant

12.20 Calcium Hardness and Calcium

Occurrence and significance : The presence of calcium (fifth among the elements in order of abundance) in water supplies results from passage thro' or over deposits of limestone, dolomite, gypsum and gypsiferous shale.

Small concentrations of $CaCO_3$ 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.

Materials and methods :

The atomic absorption method is accurate means of determining calcium. The EDTA titration method gives good result for routine.

EDTA Titrimetic method :

Principle

When di-sodium EDTA salts is added to water containing both Calcium and Magnesium, it combines first with the calcium. Calcium can be determined directly with EDTA, when the pH is made sufficiently high that the magnesium is largely precipitated as the hydroxide and an indicator is used that combines with calcium only. When pH becomes 12 to 13 with help of NaOH, all the calcium has been complexed by the EDTA, that moment particular indicators gives colour change.

Interference : Strontium and barium give positive interference.

- Orthophosphate precipitate Ca at high pH
- Alkalinity > 300 ppm may cause indistinct end point in hard water

Reagents

- 1.0 N NaOH
- Murexide Indicator - (Ammonium purpurate) 200 mg Murexide grond with 100g solid NaCl
- STD EDTA (0.01M) : As per T.H.
  0.01M = 400.8 µg Ca/1.0 ml

Procedure

- Generally 50.0 ml sample portion is taken
- Add 2.0 ml NaOH (1 N)
- Add 0.1 to 0.2g indicator mixture
- Add EDTA Titrant slowly with continuous stirring to proper end point (pink to purple)

- Check end point by 1 to 2 drops in excess

Calculation :

$$\text{mg Ca/l} = \frac{A \times B \times 400.8}{\text{ml Sample}}$$

Calcium Hardness

$$\text{as mg } CaCO_3\text{/l} = \frac{A \times B \times 1000}{\text{ml Sample}}$$

Where,

A = ml titrant for sample

B = mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant at the calcium indicator end point

12.21 Magnesium

Occurrence : Mg ranks eighth among the elements in order of abundance and is a common constituent of natural water. Mg is a important contributors to the hardness. Mg-salts break down when heated forming scale in boilers. Concentration > 125ppm also can have a cathartic and diuretic effect.

Materials and methods :

Direct determination can be made with the atomic absorption spectrometer.

Magnesium may be estimated as the difference between hardness and calcium as $CaCO_3$ calculations :

mg Mg/l - [Total hardness (as $CaCO_3$ mg/l) - Calcium hardness (as $CaCO_3$ mg/l)] X 0.243.

12.22 Sulphate

Occurrence : Sulphate is widely distributed in natural water. Sodium sulphate and magnesium sulphate exert a cathartic reaction.

Materials and methods :

The turbidimetric method is applicable in the range of 1 to 40 mg/l Sulphate.

Principle : Sulphate ion is precipitated in an acetic acid medium with $BaCl_2$ to form $BaSO_4$ crystals of uniform size. Light absorbance of the $BaSO_4$ susp. is measured by a photometer and the sulphate concentration is determined by comparison of the reading with standard curve.

Interference : Colour or suspended solids in large amounts will interfere. To correct this, blank should be run.

Apparatus :

- Magnetic stirrer
- Nephelometer

Reagents :

- Buffer solution - A: Dissolve 30g $MgCl_2.6H_2O$ 5.0 g. sodium acetate ($CH_3COONa.\ 3H_2O$), 1 g KNO_3 and 20 ml acetic acid in 500 ml distilled water and make up to 1 litre
- Barium chloride powder
- Standard Sulphate Solution : Dissolve 0.1479g anhydrous Na_2SO_4 in distilled water and dilute to 1000 ml; 1.0 ml = 100 µg SO^{-2}_4 .

Procedure :

- Take 100 ml sample
- Add 20 ml buffer solution - A & mix in stirring apparatus
- While stirring, add a spoonful of $BaCl_2$ crystals and begin timing immediately. Stir for 60 ± 2 S at constant speed
- Allow ppts to form for 5 min.
- Pour solution into absorption cell and measure N.T. units
- Estimate SO^{-2}_4 concentration by comparing NTU with calibration curve

Calculation :

$$\text{mg } SO^{-2}_4/l = \frac{\text{mg } SO^{-2}_4 \times 1000}{\text{ml sample}}$$

12.23 Chloride

Chloride, in the form of chloride (Cl^-) ion, is one of the major inorganic anions in water and waste water. Some waters containing 250 mg/l Cl^- may have a detectable salty taste if the cation is sodium. On the other hand, a typical salty taste may be absent in waters containing as much as 1000 mg/l when the predominant cations are calcium and magnesium. Along the sea coast, chloride may be present in high concentrations because of leakage of salt water in to the sewerage system.

A high Cl^- content may harm metallic pipes and structures, as well as growing plants.

Principal :

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 chromate is formed.

Materials and Methods

Chlorides : The argentometric method is suitable for use in relatively clear water.

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

Interference: Sulfide, thiosulphate and sulphite ions can be removed by treatment with H_2O_2. Orthophosphate (>25 ppm) interferes by precipitating as silver phosphate. Iron (>10 ppm) mask the end point.

Regeants :

- Std. $AgNO_3$ titrant : 0.0141 M (0.0141 N): Dissolve 2.395 g. $AgNO_3$ in Di.H_2O and dilute to 1000 ml. Standardize against NaCl, 1.0 ml = 500 µg Cl^- Store in brown bottle.
- Potassium chromate indicator solution: Dissolve 50 gm. K_2Cro_4 in a little di.H_2O. Add $AgNO_3$ solution until a definite red ppts is formed let stand 12 h, filter and dilute to 1 litre.
- Standard sodium chloride : 0.0141 M(0.0141N). Dissolve 824.0 mg Nacl (dried at 140°C) in di H_2O and dilute to 1 Lt.; 1.0 ml = 500 µg Cl^-

Regeants for interference removal :

- Aluminium hydroxide susp:
- Phenolphthalein indicator :
- NaOH, 1 N
- H_2SO_4, 1 N
- H_2O_2, 30%

Procedure :

- Take suitable portion for titration (Generally 50.0 ml) Titrate in pH range 7 to 10, Adjust pH with NaOH or H_2SO_4, if necessary
- Add 1.0 ml K_2CrO_4 indicator solution
- Titrate with Std. $AgNO_3$ until Piukish yellow end point. (Be consistent in end - point recognition

  NOTE : If sample is highly coloured, Add 3.0 ml $Al(OH)_3$ Susp., mix. let settle and filter.
- If sulphide, sulphite or thiosulphate is present, Add 1.0 ml H_2O_2, stir for 1 min

Calculation : $$\text{mg } Cl^-/l = \frac{(A-B) \times N \times 35450}{\text{ml of Sample}}$$

Where,

A = ml titration for sample

B = ml titration for Black

N = Normality of $AgNO_3$

NOTE: Normality X 35450 = 499.845 = 500 therefore, to make easy calculation.

Normality of $AgNO_3$ is taken 0.0282 in practise, so that - (i e. double)

Normality X 35450 =

0.0282 X 35450 = 999.69 = 1000

Now, it is general consideration that B = ml titration for Blank is almost 0.0 ml and sample portion is 50.0 ml

mg Cl^-/l = $\frac{\text{Reading X 1000}}{50}$ = Reading X 20

12.24 Nitrate

Nitrates represents the most highly oxidized phase in the Nitrogen cycle and normally reaches imp. concentration in the final stage of biological oxidation. It generally occurs in trace quantities in surface water supplies but may attain high levels in some ground waters. In excessive amount, it contributes to the illness known as infant methamoglobinemia.

Phenol - disulphonic acid method :

Principle : The yellow colour produced by the reaction between Nitrate and Phenoldisulphonic acid obeys Beer's law up to at least 12 ppm N at a wavelength of 480 n.m. when a light path is of 1.0 c.m. At a wavelength of 410 n.m. the point of maximum absorption, determination may be made up to 2 mg/l with the Same cell path.

Interference : The PDA method is subject to severe chloride interference, necessitating complete chloride removal for correct result.

Apparatus :

Spectronic - 20, for use at 410 n.m. providing a light path of 1.0 c.m.

Reagents :

- Commercially good PDA reagent available in market.
- Stock Nitrate solution. Dissolve 721.8 mg anhydrous KNO_3 and dilute to 1000 ml with Di.H_2O. This solution contain 100 mg/l N.
- STD Nitrate Solution. Evaporate 50.0 ml stock nitrate solution to dryness and dissolve the residue by rubbing with 2.0 ml PDA Regent and dilute to 500 ml with Di.H_2O.

  1.0 ml = 10.0 µg N - 44.3 µg NO_3

  Procedure :

- Take 1.0 ml sample in clean dried beaker.
- Evaporate to dryness.
- Rub the residue thoroughly with 2.0 ml PDA Regent to insure dissolution of all solids.
- Dilute to 15.0 ml with Di.H_2O and add with stirring, about 6 to 7 ml NH_4OH until maximum colour is developed.
- Dilute to 25.0 ml and mix
- Measure O.D. at 410 n.m. using Blank for 100% transmission
- From Std. curve, observe the µg N

Calculation :

$$\text{mg/l (Nitrate as N)} = \frac{\mu g \text{ Nitrate N}}{\text{ml, sample}}$$

12.25 Fluoride

A Fluoride conc. of 1.0 ppm in drinking water reduce dental caries without harmful effects on health. Fluoride in excess cause fluorosis, which may occur when the fluoride level exceeds the recommended limits in some community, where no other source is available other than high fluoride source, defluoridation is required by Nalgonda technique.

Materials and Methods :

Electrode and colorimetric method (SPADNS) are the most satisfactory. These methods are subject to errors by interfering agents like Alkalinity, Al^{+3}, Cl^{-}, chlorine, Iron, SO_4^{-2}, PO^{-3}_4etc. so, it becomes necessary to distilled the sample. When interfering ion are low in concentration, direct determination can be made.

The electrode method is suitable for fluoride concentration from 0.1 to 10.0ppm while SPADNS methods has an analytical range of 0.0 to 1.40 ppm fluoride. A curve developed from standards is used for determination of F from the sample. Preferably use polythene bottles for collection and storing sample for fluoride analysis.

Spadns Method

Principle : Method is based on reaction between F and Zirconium-dye lake. Fluoride reacts with the dye-lake, dissociating a portion of it in to a colourless complex anion $(ZrF_6)^{-2}$ and the dye. As the amount of fluoride increases, the colour produced becomes progresively lighter. Generally, distillation is necessary when samples are coloured or turbid or heavy interference.

Precautions : Volumetric measurements of sample and reagents is extremely important to analytical accuracy. Samples and STDS should be at same temperature.

Apparatus : Spectrophotometer - for use at 570 nm providing a light path of atleast 1 cm.

Reagents :

- STD. F Solution : Dissolve 221.0 mg anhydrous NaF in di.H_2O and dilute to 1 lt., 1.0ml = 100 µg F^{-}. This is a STOCK F Solution, from this make 10 times dilution i.e. 1.0 ml = 10µg F.
- SPADNS Solution -> Dissolve 958 mg SPADNS in di.H_2O and dilute to 500 ml. [Stable for 1 yr. and protect from sum light).
- Zirconyl-acid reagent : Dissolve 133 mg Zirconyl chloride octahydrate $ZrOCl_2$. $8H_2O$ in about 25 ml di.H_2O. Add 350 ml conc. HCl and dilute to 500 ml with Di.H_2O.

- Acid Zirconyl - SPADNS reagent : Mix equal volume of SPADNS solution and Zirconyl - acid reagent. The combine solution is stable for 2 yrs.
- Reference Solution : Add 10 ml SPADNS solution to 100 ml Di.H_2O. Dilute 7.0ml conc HCl to 10 ml and add to diluted SPADNS solution. This solution used for setting the instrument reference point i.e. (0.0) Zero O.D. (Stable for 1 yr.)

Procedure :

STD curve preparation.

- Prepare F Std. in range of 0.0 to 1.40ppm by diluting Std. F to 50 ml portion with Di.H_2O.
- Add 10.00 ml mixed Acid-Zirconyl - SPADNS Reagent and mix well.
- Set Spectronic - 20 to Zero O.D. with reference solution.
- Obtain absorbance reading of standards at 570 nm.
- Plot curve of µg F^- Vs O.D. (NOTE: Fresh curve for fresh reagents)
- Measure F^- in same manner.

Calculation :

$$mg\ F^-/l = \frac{A}{ml\ sample} \times \frac{B}{C}$$

Where,

A = µg F^- determined from plotted curve

B = Final volume of diluted sample

C = Volume of diluted sample used for colour development. ml.

12.26 Alkalinity

Alkalinity of a water is it's acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with end-point pH used. Alkalinity is a measure of an aggregate property of water. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate and hydroxide content, it is taken as an indication of the concentration of these constituents. Alkalinity in excess of alkaline earth metal concentration is significant in determining the suitability of a water for Irrigation.

Titration method :

Principle : Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes reacts with addition of Std. acid. Thus, alkalinity depends on end-point pH used. "Phenolphthalein alkalinity" is the term used for the quantity measured by titration to pH-8.3 using phenolphthalein as indicator.

While methyl-orange alkalinity is a quantity measured by titration at pH - 4.5.

Reagents :

- Standard Sulphuric acid titrant : 0.02 N- (Prepare stock solution approximately 0.1 N by diluting 2.8 ml cone. H_2SO_4 to 1 litre). Dilute 200 ml of stock (0.1 N) solution to 1 litre, 1.00 ml = 1.0 mg $CaCO_3$.
- Sodium carbonate solution (0.02 N) dissolve 1.060 g anhydrous Na_2CO_3 (primary Std. grade) oven dried at 140°C and dilute to 1 litre.
- Phenolphthalein solution, alcoholic pH - 8.3 indicator.
- Methyl - Orange indicator.

Procedure :

Phenolphthalein alkalinity :

- Take 50.0 ml sample
- Add 2 drops of phenolphthalein indicator
- Titrate with 0.02N H_2SO_4 untill the pink colour just disappears.

Calculation

mg/l, Phenolphthalein alkalinity = $\frac{A \times N \times 50000}{\text{ml sample}}$ as $CaCO_3$

Where, A = ml, standard acid used

N = Normality of Standard acid

SO, mg/l 'P' Alkalinity = $\frac{A \times 0.02 \times 50000}{\text{ml sample}} = \frac{\text{ml titrant} \times 1000}{\text{ml sample}}$

Total or methyl orange alkalinity :

- Take 50.0ml sample or use the sample, in which phenolphthalein alkalinity has been determined.
- Add 2 drops of methyl orange indicator.
- Titrate with 0.02 N H_2SO_4 untill colour changes from yellow to faint orange.

Calculation :

mg/l total or methyl orange alkalinity as $CaCO_3$ = $\frac{\text{ml titrant} \times 1000}{\text{ml, Sample}}$

Alkalinity relationship :

Result of titration	Hydroxide alkalinity as $CaCO_3$	Carbonate alkalinity as $CaCO_3$	Bicarbonate concentration as $CaCO_3$
P=O	O	O	T
P<½ T	O	2P	T-2P
P=½ T	O	2P	O
P>½ T	2P-T	2(T-P)	O
P=T	T	O	O

Where, P = Phenolphthalein alkalinity, T = Total Alkalinity

12.27 Iron

Occurrence and significance : In filtered sample of oxygenated surface waters iron concentration seldom reach 1 ppm. while some ground waters may contain considerably more Iron. Iron in water can cause staining of laundry and porcelain. A bittersweet astringent taste at levels above 1.0 ppm. In water samples Iron may occur in true solution, in a colloidal state, in inorganic or organic iron complexes or in relatively course suspended particles. It may be either ferrous or ferric, suspended or dissolved Iron may come from a metal cap used to close the sample bottle.

Method : Phenanthroline method.

Principle : Iron is brought in to solution, reduced to the ferrous state by boiling with acid and hydroxylamine and treated with 1, 10-Phenanthroline at pH 3.2 to 3.3. Three molecules of Phenanthroline chelate each atom of ferrous iron to form an orange-red complex, the colour solutions obeys Beer's law it's intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures rapid colour development in the presence of an excess of Phenanthroline.

Interference : CN^-, NO_2^- and PO^{-3}_4 Cr^{+3} & $^{+6}$ Zn^{+2} when 10 times of Iron, Co and Cu when > 5 ppm and Ni > 2 ppm, Bi, Cd, Hg, Mo and Ag precipitate phenanthroline.

The initial boiling with acid converts polyphosphates to orthophosphate and removes CN^- and NO^-_2; excess hydroxylamine eliminates errors caused by excessive oxidizing agents. Excess of phenanthroline removes interference of metals.

Apparatus :

- Spectrophotometer at 510nm.
- Acid washed glass-ware.

Reagents :

Use Iron-free di.H_2O in preparation.

- Conc. Hcl
- Ammonium acetate buffer: Dissolve 250g $NH_4C_2H_3O_2$ in 150 ml water. Add 700 ml conc (glacial) acetic acid.
- Sodium acetate solution : Dissolve 200 g $NaC_2H_3O_2.3H_2O$ in 800 ml water.
- Phenanthroline solution : Dissolve 100mg 1, 10 - phenanthroline monohydrate in 100 ml water by stirring, add 2 drops of conc HCl.
- Stock Iron Solution : Slowly add 20 ml conc H_2SO_4 to 50 ml water and dissolve 1.404 g ferrous ammonium sulphate. Add 0.1 N $KMnO_4$ dropwise until a faint pink colour persists. Dilute to 1000 ml with water and mix; 1.00 ml = 200 µg Fe.
- Std. Iron solution : Prepare daily for use.
  Pipet 50.00 ml stock solution in to 1000 ml volumetric flask and dilute to mark with Di.H_2O; 1.00 ml = 10 µg Fe.
- Hydroxylomine solution : Dissolve 10 g $NH_2OH.HCl$ in 100 ml water.

Procedure :

Total Iron :

- Mix sample thoroughly and measure (take) 50.0 ml sample in flask
- Add 2.0 ml conc HCl and 1.0 ml $NH_2OH.HCl$ Solution
- Add a few glass beads and heat to boiling (To insure dissolution of all the Iron, continue boiling until volume is reduced to 15 to 20 ml)
- Cool to room temperature and transfer to 50.0 ml volumetric flask
- Add 10.0 ml $NH_4C_2H_3O_2$ buffer solution and 4.0 ml Phenanthroline solution and dilute to mark with $Di.H_2O$
- Mix thoroughly and allow at least 10' to 15' for maximum colour development
- Dissolved Iron : filter the sample through 0.45 μm filter and follow the above procedure.
- Read the Iron at 510 n.m. (N.B.: If sample contain colour or turbidity, run a parallel blank, without phenanthroline) using light path 1 cm.
- Prepare standard curve selectin a series of standards covering the range 50-200 μg Fe.
- Calculate Iron from Std. curve calculation:

$$\text{mg Fe/l} = \frac{\mu g \quad Fe}{\text{ml sample}}$$

12.28 Manganese

Although Manganese in ground water generally is present in the soluble divalent ionic form because of the absence of oxygen, part or all of the Manganese in a water treatment plant may be in higher valence State. Determination of total Manganese does not differentiate the various valence State. The heptavalent permanganate ion is used to oxidize manganese and/or organic matter causing taste.

There is evidence that Manganese occurs in surface water both in suspension in the quadrivalent State and in the trivalent state in a relatively stable, soluble complex. Although rarely present in excess of 1 mg/l, Mn imparts objectionable and tenacious stains to laundry and plumbing fixtures.

Method : persulphate method

Persulphate method is preferred because the use of mercuric ion can control interference from a limited chloride ion concentration.

Principle : persulphate oxidation of soluble manganous compounds to form permanganate is carried out in the presence of silver nitrate.

Interference : 0.1g Cl^- in 50.0ml sample can be prevented from interfering by adding 1g $HgSO_4$, Br^- and I^- also Interfere.

Sample that have been exposed to air may give low results due to precipitation of MnO_2. Add 1.0 drop 30% H_2O_2 to redissolve precipitated Mn.

Apparatus :

Spectrophotometer, for use at 525 nm, providing light path of 1 cm.

Reagent :

- Special reagent : Dissolve 75g $HgSO_4$ in 400 ml cone HNO_3 and 200 ml Di.H_2O. Add 200 ml 85% H_3PO_4 and 35 mg $AgNO_3$. Cool, dilute to 1 litre.
- Ammonium persulphate - $(NH_4)_2\ S_2\ O_8$ - Solid
- STD Mn Solution : Prepare 0.1 N $KMnO_4$ Solution by dissolving 3.2g $KMnO_4$ in Di.H_2O and making up to 1 lt.. heat for several hrs. near the boiling point, than filter thro' rough filter paper and standardize against sodium-oxalate as follows ;
  - Weigh several 100 to 200 mg sample of $Na_2C_2O_4$ in beaker.
  - Add 100 ml Di.H_2O and dissolve
  - Add 10 ml 1+1 H_2SO_4 and heat rapidly to 90°C to 95°C
  - Titrate rapidly with the $KMnO_4$ solution with stirring
  - Titrate until slight pink end point colour that persists for at least 1 min. (N.B.: temp. should not come down during titration).
  - Run a blank on Di.H_2O and H_2SO_4

    $$\text{Normality of } KMnO_4 = \frac{\text{g } Na_2C_2O_4}{(A-B) \times 0.06701}$$

    Where,

    A = ml titrant for sample

    B = ml titrant for blank

    Average result of several titrations calculate volume of this solution necessary to prepare 1 litre of solution so that 1.00 ml = 50.0 µg Mn as follows :

    $$\text{ml } KMnO_4 = \frac{4.55}{\text{normality of } KMnO_4}$$

    To this volume, add 2 to 3 ml conc. H_2SO_4 and $NaHSO_3$ solution dropwise, with stirring, until the permanganate colour disappears. Boil to remove excess SO_2, Cool and dilute to 1000 ml with Di.H_2O. Dilute this solution further to measure small amounts of manganese.
- 30% H_2O_2
- Conc. HNO_3
- Conc. H_2SO_4
- Sodium Oxalate - primary standard
- sodium bisulfite - Dissolve 10g $NaHSO_3$ in 100 ml Di.H_2O

Procedure :

- Take suitable sample portion (80.0 ml)

- Add 5.0 ml special reagent + 1 drop H_2O_2
- Dilute to 90.00 ml Approx.
- Add 1g $(NH_4)_2 S_2 O_8$, bring to a boil
- Boil for 1 min.(Do not heat on a water bath)
- Remove from heat source
- Let stand 1 min, than cool under the tap (Boiling too long results in decomposition of excess persulphate and subsequent loss of permanganate colour, cooling too slowly has the same effect)
- Dilute to 100 ml with Di.H_2O and mix
- Prepare standards containing 0, 5.0,.....1500 µg Mn by treating in the same way
- Read the O.D. at 525 n.m using light path 1 cm and calculate Mn from Std. curve.

Calculation :

$$\text{mg Mn/l} = \frac{\text{µg Mn (in 100ml final vol)}}{\text{ml sample}}$$

12.29 Silica

Silica ranks next to oxygen in abundance in the earth's crust. Degradation of silica containing rocks results in the presence of silica in natural water.

The silica (SiO_2) content of natural water most commonly is in the 1 to 30 ppm. range, although concentration as high as 100 ppm are not unusual and concentration exceeding 1000 ppm are found in some brackish waters and brines.

Methodology : Molybdosilicate method

This method is recommended for relatively pure water containing from 0.4 to 25ppm SiO_2. Same should be collected in polyethylene bottles, plastics or hard rubber. Borosilicate glass is less desirable choice, especially when water has pH > 8.0, in these cases a significant amount of silica in the glass can dissolve.

Principle :

Ammonium molybolate at pH approx. 1.2 reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molydophosphoric acid but not the molybdo silicic acid. The intensity of yellow colour is proportional to the concentration of "molybdate reactive" silica. "Molybdate unreactive silica" can be converted to "molybdate - reactive silica" by heating or fusing with alkali.

Interferencc : Avoid using glass-ware as much as possible as it contribute silica; tannin, large amount of Iron, Colour, turbidity sulfide and phosphate interfere. Treatment with oxalic acid eliminates interference from phosphate and decreases interference from tannin.

Apparatus :

Spectrophotometer for use at 410nm.

Reagents :

- Hydrochloric acid HCl 1 + 1
- Ammonium molybdate reagent : Dissolve 10 g $(NH_4)_6 Mo_7O_{24}$. 4 H_2O is di.H_2O with stirring and gentle warming and dilute to 100 ml. Adjust the pH 7 to 8 with silica-free NaOH and store in polythylene bottle.
- Oxalic acid : Dissolve 7.5 g $H_2C_2O_4.H_2O$ in Di. H_2O and dilute to 100 ml.
- STOCK Silica solution : Dissolve 4.73g sodium metasilicate nonahydrate Na_2SiO_3. $9H_2O$ in di.H_2O and dilute to 1000 ml; store in plastic bottle.
- Standard silica solution : Dilute 10.0 ml stock solution to 1000ml with Di.H_2O; 1.00 ml : 10.0 µg SiO_2. Store in plastic bottles.

Procedure :

- To 50.0 ml sample add in rapid succession 1.0 ml 1 + 1 HCl and 2.0 ml ammonium molybdate reagent.
- Mix with vigourous shaking and let stand for 5 to 10 min.
- Add 2.0 ml oxalic acid solution and mix thoroughly.
- Read after 2 min but before 15 min. (measure time-from addition of oxalic acid) at 410 n,m. using light path 1 cm.
- Prepare calibration curve selecting a series of standards covering the range 200 to 1300 µg SiO_2 setting photometer at zero absorbance with Di.H_2O.
- Calculate SiO_2 from Std. curve

  Calculation :

$$\text{mg } SiO_2/l = \frac{\mu g\ SiO_2 \text{ (in 55 ml final vol)}}{\text{ml sample}}$$

12.30 Boron

Although it is an essential element for plant growth, boron in excess of 2.0 mg/l in irrigation water is deleterious to certain plants. Drinking waters rarely contain more than 1 mg/l and generally less then 0.1 mg/l, concentration considered innocuous for human consumption. The ingestion of large amounts of boron can affect the central nervous system. Protracted ingestion may result in a clinical syndrome known as borism.

Selection of method : The curcumin method is applicable in the 0.1 to 1.0 mg/l range. Storage of sample in polyethylene bottles is preferable.

Curcumin method :

Principle : When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-coloured product called rosocyanine is formed. The rosocyanine is taken up in a suitable solvent and red colour is compared photometrically.

Interference :

NO_3 - N concentration above 20 mg/l interfere. Significantly high results are possible when the total of Ca and Mg hardness exceeds 100ppm. This interference springs from the insolubility of the hardness salts in 95% ethanol and consequent turbidity in the final solution. Filter the final solutin or pass the original sample thro' a column of strongly acidic cation - exchange resin in the hydrogen form to remove interfering cations.

Apparatus :

- Spectrophotometer - for use at 540 n.m.
- Evaporating dishes : 100 to 150 ml capacity of high silica glass.
- Water bath set at 55 ± 2°C.
- Glass-stoppered volumetric flasks - 25 and 50 ml capacity.

Reagents :

- STOCK Boron solution : Dissolve 571.6 mg anhydrous boric acid H_3BO_3 in Di.H_2O and dilute to 1000 ml; 1 ml = 100 µg B.
- STD Boron Solution : Dilute 10 ml stock Boron solution to 1000ml with Di.H_2O. 1.0 ml = 1.00 µg B.
- Curcumin reagent : Dissolve 40 mg finely ground curcumin and 5.0g oxalic acid in 80 ml 95% ethyl alcohol. Add 4.2 ml conc. HCl, make up to 100 ml with ethyl alcohol in 100ml vol. flask. (N.B. : isopropyl alcohol 95% may be used in place of ethyl alcohol).
- Ethyl or isopropyl alcohol 95%.
- Reagents for removal of high hardness and cation interference.
  - Strongly acidic - cation - exchange resin
  - Hydrochloric acid, HCl, 1 + 5

Procedure :

Preparation of calibration curve : Pipet O (Blank), 0.25, 0.50, 0.75 and 1.00 µg Boron in to evaporating dishes of the same type, shape and size.

- Add Di.H_2O to bring total Vol. to 1.0 ml.
- Add 4.0 ml curcumin reagent to each and mix gently.
- Float dishes on a water bath set at 55 ± 2°C and let them remain for 80 min. (Keep drying time constant for Std. and samples).
- After dishes cool to room temperature, add 10 ml 95% iso-propyl alcohol (ethyl alcohol) to each dish and stir gently with a polyethylene rod to insure complete dissolution of the red-coloured product.
- Wash content of dish in to 25 ml vol. flask using 95% ethyl (iso-propyl) alcohol.
- Make up the vol. up to mark with 95% isoprophyl (ethyl) alcohol.
- Mix thoroughly by inverting.

- Read absorbance at 540 nm (within 1 hr. of drying samples). (N.B. : Use 1.0 ml sample, when 0.1 to 1.00 mg B/l concentration is there - If the final solution is turbid, filter through filter paper.

  Calculation :

  $$\text{mg B/l} = \frac{A_2 \times C}{A1 \times S}$$

  Where,

  A1 = absorbance of Std.

  A2 = absorbance of Sample

  C = μg B in Standard taken

  S = ml sample

12.31 Chemical Oxygen Demand

The COD is used as measure of the oxygen equivalent of the organic matter content of the sample that is susceptible to oxidation by a strong chemical oxidant.

The dichromate reflux method is preferred because of superior oxidizing ability, applicability to wide variety of samples and ease of manipulation.

interference : Volatile straight chain aliphatic compounds are not oxidized to any appreciable extent. This failure occurs partly because volatile organics are present in the vapor-space and do not come in contact with the oxidizing liquid. These compounds are oxidized more effectively when silver sulphate (Ag_2SO_4) is added as a catalyst.

A difficulties caused by the presence of the halides can be overcome largely, by complexing with H_gSO_4 before the refluxing procedure.

Sample should be preserved by acid to pH $\leq$ 2. using conc. H_2SO_4

Method : Open reflux method.

Principle : Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of $K_2Cr_2O_7$. After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous aommonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent. Keep ratios of regent weights, volumes and strengths constant when sample vol. other than 50.0 ml are used. The standard reflux time is 2 Hrs.

Apparatus : Reflux apparatus.

Reagents :

- Std. $K_2Cr_2O_7$ Solution: 0.25 N (0.0417 M). Dissolve 12.259g $K_2Cr_2O_7$, primary Std. grade previously dried at 103°C for 2h, in di.H_2O and dilute to 1000 ml.

- Sulphuric acid reagent : Add Ag_2SO_4 technical grade crystal or powder to conc. H_2SO_4 at th rate of 5.5g Ag_2SO_4/Kg H_2SO_4, let stand 1 to 2 days to dissolve Ag_2SO_4.
- Ferroin indicator solution : Dissolve 1.485g 1, 10 phenanthroline monohydrate and 695 mg $FeSO_4$. $7H_2O$ in di.H_2O and dilute to 100 ml.
- Standard ferrous ammonium sulphate (FAS) titrant (0.25 M) - approximately : Dissolve 98 g $Fe(NH_4)_2$ $(SO_4)_2$. $6H_2O$ in Di.H_2O. Add 20 ml Conc. H_2SO_4, cool and dilute to 1000 ml. Standardize this solution daily against Std. $K_2Cr_2O_7$ solution as follows :

  Dilute 10.0 ml Std. $K_2Cr_2O_7$ to about 100 ml, Add 30 ml conc. H_2SO_4 and cool. Titrate with FAS using ferroin indicator.

  Molarity of FAS solution = ml, volume $\frac{0.0417M/K_2Cr_2O_7 \text{ titrated}}{\text{Vol FAS used in titration, ml}}$ X 0.25

- Mercuric sulphate, $HgSO_4$ powder

Procedure

- Take 10.0 ml STD $K_2Cr_2O_7$ solution
- Add 1 g $HgSO_4$ and several glass beads.
- Add conc H_2SO_4 having Ag_2SO_4 (as required to maintain the ratio - generally 30 ml).
- Add suitable sample portion with constant swirling and cooling.
- Attach flask to condenser and turn on cooling water.
- Reflux for 2 Hrs.
- Cool and wash down condenser with Di.H_2O.
- Cool to room temperature.
- Disconnect reflux condenser.
- Titrate excess $K_2Cr_2O_7$ with FAS using 2 to 3 drops ferroin indicator.
- End point is the sharp colour change from blue-green to raddish brown.

Calculation :

$$\text{COD as mg } O_2/l = \frac{(A-B) \times M \times 8000}{\text{ml sample}}$$

Where,

A = ml FAS used for blank

B = ml FAS used for sample

M = Molarity of FAS

12.32 Zinc

Zinc is an essential and beneficial element in human growth. Concentration above 5ppm can cause a bitter astringent taste and an opalescence in alkaline waters. Zinc most

commonly enters the domestic water supply from deterioration of galvanized iron and dezincification of brass. Dithizone method - I is intended for potable water.

Dithizone method - I :

Principle : Nearly 20 metals can react with dithizone to produce coloured coordination compounds. These dithizonates are extractable in to organic solvents such as carbon tetrachlorides (CCl_4).

Most interference in the Zinc-dithizone reaction can be overcome by adjusting pH to 4.0 to 5.5 and by adding sufficient $Na_2S_2O_3$.

The duration and vigor of shaking, the volume of sample, sodium thiosulfate and dithizone and the pH should be kept constant.

Interference :Interference from bismuth cadmium, cobalt, copper, gold, lead, mercury nickel, palladium, silver and stannous tin in the small quantities found in potable water is eliminated by complexing with $Na_2S_2O_3$ and by pH adjustment.

Apparatus :

- Spectrophotometer : for use at 535 nm
- Nessler tubes
- Separatory funnels : capacity 125 ml squibb form, preferably with inert TFE stopcocks.
- Glass-ware : rinse all glass-ware with 1 + 1 HNO_3 and water.

Reagent :

- Zinc free water : Di.H_2O-Zn free.
- Stock zinc solution : Dissolve 100.0 mg 30-mesh Zinc metal in a slight excess of 1 + 1 HCl, about 1.0 ml is required. Dilute to 1000ml with water.

  1.0 ml = 100 µg Zn
- Std. Zinc solution : Dilute 10 ml stock Zinc solution to 1000ml with water

  1.0 ml = 1.00 µg Zn
- 0.02 N HCl : Dilute 1.0 ml conc. HCl to 600 ml with water.
- 2 M sodium acetate : Dissolve 68g $NaC_2H_3O_2$. $3H_2O$ and dilute to 250 ml with water.
- Acetic acid : 1 + 7
- Acetate buffer solution : Mix equal Vol. of 2 M sodium acetate solution and 1 + 7 acetic acid solution extract with 10 ml. portions of dithizone solution - I until the last extract remains greens, then extract with CCl_4 to remove excess dithizone.
- Sodium thiosulfate solution : Dissolve 25g $Na_2S_2O_3$_ $5H_2O$ in 100 ml water. Purify by dithizone extraction.
- Stock dithizone solution (CCl_4) 125mg dithizone/500ml CCl_4 : Dissolve 125 mg dithizone in 50 ml $CHCl_3$ and filter thro' whatman filter paper. Receive filtrate in a 1000 ml separatory funnel, wash beaker with two 5 - ml portion $CHCl_3$ and filter.

Wash paper with three 5 ml portions $CHCl_3$ adding the last portion dropwise to edge of paper.

Add 200 ml 1 + 99 NH_4OH to separatory funnel and shake moderately for 1 min. Let layers separate, swirling funnel gently to sub-merge $CHCl_3$ droplets held on surface of aqueous layer. Transfer $CHCl_3$ layer to 500 ml separatory funnel, retaining the orange-red aqueous layer in the 1000 ml funnel. Repeat extraction of $CHCl_3$ layer with 200 ml 1 + 99 NH_4OH transferring $CHCl_3$ layer to another 500ml separatory funnel. Transfer aqueous layer to 1000 ml funnel holding the first extract. Repeat extraction with third 200 ml portion 1 + 99 NH_4OH. Discard $CHCl_3$ layer, transfer aqueous layer to 1000 ml funnel. To the combined extract add 1 + 1 HCl in 4 ml portions, mixing after each addition until dithizone precipitates and no longer orange-red colour in solution extract precipitated dithizone with four 25-ml portions CCl_4, dilute combined extract to 500 ml with CCl_4.

1.0 ml = 250 µg dithizone

- Dithizone solution - I : Dilute 40 ml stock dithizone solution (CCl_4) to 100 ml with CCl_4 prepare daily.
- Dithizone solution - II : Dilute 10 ml dithizone solution - I to 100 ml with CCl_4 prepare daily.
- CCl_4 : carbon tetrachloride -> ACS grade
- Sodium citrate solution -> Dissolve 10g $Na_3C_6H_5O_7.2H_2O$ in 90 ml water.

Procedure :

Preparation of colourimetric standards :

To a series of thoroughly cleansed 125-ml squibb separatory funnels, add 0, 1.00, 2.00, 3.00, 4.00 and 5.00 ml Std. Zn solution to provide Std. containing 0, 1.00, 2.00, 3.00, 4.00 and 5.00 µg Zn respectively. Bring each vol. up to 10.0 ml by adding water. To each funnel add 5.0 ml acetate buffer and 1.0 ml $Na_2S_2O_3$ solution and mix. The pH should be between 4.0 and 5.5. To each funnel add 10.0 ml dithizone solution - II, stopper and shake vigorously for 4.0 min. Let layers separate, dry inside of stem below stopcock of funnel with strips of filter paper and run lower (CCl_4) layer in to a clean, dry Nessler tube, measure O.D. of red colour of zinc dithizonate at 535 nm or the green colour of unreacted dithizone at 620 nm [N.B. : set photometer at 100% transmittance with the blank if 535 nm is selected. If 620 nm is used, set blank at 10% transmittance] plot a calibration curve and follow the same procedure for sample.

Calculation -> $\text{mg Zn/l} = \frac{\mu g\ Zn}{\text{ml sample}}$

12.33 Cyanide

The great toxicity to aquatic life of molecular HCN is well-known, it is formed in solutions of cyanide by hydrolytic reaction of CN^- with water. The toxicity of CN^- is less than that of HCN.

Selection of method :

Total cyanide after distillation : After removal of interfering substances the metal cyanide is converted to HCN gas, which is distilled and absorbed in NaOH solution. Sulfides, fatty acids and oxidizing agents are removed by special procedures. Most other interfering substances are removed by distillation. The importance of the distillation procedure can not be overemphasized.

Interference :

Sulfide interference can be overcome by lead acetate.

Fatty acid can be removed by extraction method.

Carbonate can be removed by use of $Ca(OH)_2$.

Nitrite and Nitrate can be avoid by addition of 2g sulfamic acid to the sample before distillation.

Alternate procedure i.e. the strong acid distillation procedure uses concentrated acid with $MgCl_2$ to dissociate metal cyanide complexes.

Total cyanide after distillation :

Hydrogen cyanide (HCN) is librated from an acidified sample by distillation and purging with air. The HCN gas is collected by passing it through on NaOH scrubbing solution. Cyanide concentration in the scrubbing solution can be determined by titration.

Apparatus : CN^- distillation apparatus includes.

- Boiling flask - 1 litre with inlet tube and provision for water cooled condenser
- Gas absorber
- Heating element
- Ground glass ST joints
- Suction pump

Reagents :

- 1 N NaOH solution : Dissolve 40 g NaOH in water and dilute to 1 Lt.
- $MgCl_2$ Reagent : Dissolve 510 g $MgCl_2$ $6H_2O$ in water and dilute to 1 lt.
- Sulphuric acid H_2SO_4 : 1 + 1.
- $PbCO_3$, powdered.
- Sulfamic acid, powdered.

Procedure :

- Add 200 ml sample to the boiling flask.
- Add 10ml NaOH solution to the gas scrubber and dilute with di.H_2O to obtain an adequate liquid depth in the absorber.

- Connect the train, consisting of boiling flask, air inlet, flask, condenser, gas washer and suction flask trap.
- Adjust suction so that approximately 1 air bubbles/s enter the boiling flask. This air rate will carry HCN gas from flask to absorber and prevent a reverse flow - maintain air flow throughout the reaction.
- Add 2g sulfamic acid thro' air inlet tube and wash down with Di.H_2O.
- Add 50ml 1 + 1 H_2SO_4 thro' the air inlet tube and Rinse with Di.H_2O and let air mix flask contents for 3 min.
- Add 20 ml $MgCl_2$ thro' air inlet tube and wash down with di.H_2O.
- Heat with rapid boiling and reflex for at least 1 hrs.
- Discontinue heating but continue air flow for 15 min.
- Cool and quantitatively transfer absorption solution to volumetric flask. Rinse absorber and it's connecting tabing sparingly with Di.H_2O and add to flask and make up the vol. to 200 ml.
- Determine CN^- by titrimetric method.

Titrimetric method :

Principle ; CN^- in the alkaline distillate from the preliminary treatment procedure is titrated with $AgNO_3$ to form soluble cyanide complex. $Ag(CN)^-_2$. As soon as all CN^- has been complexed and a small excess of Ag+ has been added, the excess Ag+ is detected by the silver-sensitive indicator, P-dimethylaminobenzalrhodamine which turns to salmon hue colour

Reagents :

- Indicator solution : Dissolve 20 mg P-dimethylaminobenzalrhodamine in 100 ml acetone.
- STD $AgNO_3$: Dissolve 3.27g $AgNO_3$ in 1 L and standardize with Std. NaCl solution using K_2CrO_4 Indicator and Adjust the titer so that

  1.0 ml $AgNO_3$ equivalent to 1.0 mg CN^-.

Procedure :

- To the 200 ml volume, add 0.5 ml indicator solution.
- Titrate with $AgNO_3$ to the first change in colour from a canary yellow to salmon hue.

Calculation :

$$\text{mg } CN^-/l = \frac{(A-B) \times 1000}{\text{ml, original sample}}$$

Where,

A = ml Std. $AgNO_3$ for sample

B = ml Std. $AgNO_3$ for Blank

Table No. 12.1

Preservation techniques of the water samples for chemical analysis

Sr. No.	Parameter	Preservation	Allowable holding time
1.	Alkalinity	Refrigerate - 4°C	24 Hrs.
2.	COD	Adjust to pH 2 with H_2SO_4	7 days
3.	Chloride	Not required	7 days
4.	Colour	Refrigeration - 4°C	24 Hrs.
5.	Cyanide	Adjust to pH 12 with NaOH	
6.	Dissolved oxygen	Determine on site	
7.	Hardness	Refrigeration - 4°C	7 days
8.	Metals	Adjust to pH with HNO_3	6 months
9.	Nitrate	Refrigeration - 4°C	24 Hrs.
10.	pH	Determine onsite or hold at 4°C	
11.	Phosphate	Hold at 4°C	24 Hrs.
12.	Turbidity	Hold at 4°C	7 days
13.	TDS	Hold at 4°C	7 days
14.	Sulphate	Hold at 4°C	7 days

Table 12·1 Water analysis methods At a glance

Sr. No.	PARAMETER	METHOD	INSTRUMENT
1.	pH	Instrumental	DIGITAL pH METER, SYSTRONICS, - INDIA
2.	Conductivity	-- DO --	Digital Conductivity Meter
3.	Turbidity	-- DO --	Systronics, India
			Nephelometer Systronics, India
4.	Sulphate	-- DO --	Nephelometer Systronics, India
5.	Alkalinity	Titrimetric	--
6.	Hardness and Calcium and Magnesium	Titrimetrice (EDTA) calculatin	--
7.	Chloride	Titrimetric (Argentometric)	--
8.	Cyanide	Titrimetric (Silver Nitrate)	--
9.	Total Dissolved Solids	Gravimetric	Monopan Balance
10.	Sodium and potassium	Flame Photometric	Flame Photometer EEL - UK
11.	Boron	Curcumine	Spectronic 20, Bausch & Lomb, USA make
12.	Fluoride	SPADNS	-- DO --
13.	Iron	Phenanthroline	-- DO --
14.	Phosphate	Stanbous chloride	-- DO --
15.	Silica	Molybdo Silicate	-- DO --
16.	Nitrate	Phenol Disulfonic Acid	-- DO --
17.	Manganese	Persulphate	-- DO --
18.	Zinc	Dithizone - 1	-- DO --
19.	COD	Dichromate Open Reflux	--
20.	Colour	Visual comparision Platinum - Cobalt scale	--
21.	Odour	Threshold Odour Test	--