Malé Declaration on Control and Prevention of Air Pollution and Its Likely Transboundary Effects for South Asia

"Wet Deposition MONITORING"
PRACTICAL MANUAL
(Water Analysis)
for
MalŒ Declaration

cpcb

Central Pollution Control Board
(Ministry of Environment & Forests)
'parivesh Bhawan', East Arjun Nagar
Delhi - 110-032 India

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National Focal Points (NFP) and National Implementing Agencies (NIA)

Bangladesh
NFP: Ministry of Environment & Forest

NIA: Department of Environment, Dhaka

Bhutan
NFP&NIA: National Environment Commission, Thimphu

India
NFP: Ministry of Environment and Forest

NIA: Central Pollution Control Board, New Delhi

Iran
NFP & NIA: Department of Environment, Tehran

Maldives
NFP & NIA: Ministry of Home Affaires, Housing & Environment, Malé

Nepal
NFP: Ministry of Population & Environment

NIA: International Center for Integrated Mountain Development, Kathmandu

Pakistan
NFP: Ministry of Environment, Local Govt. & Rural Development

NIA: Pakistan Environment Protection Agency, Islamabad

Sri Lanka
NFP: Ministry of Forest & Environment

NIA: Central Environment Authority, Colombo

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Contributors to this training material

Central Pollution Control Board	Chapter 1-14 and 16
IVL Swedish Environmental Research Institute	Chapter 15

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Malé Declaration
On

Control and Prevention of Air Pollution and its Likely Transboundary Effects for South Asia

BECKGROUND INFORMATION

In a meeting of SACEP (South Asia Cooperative Environment Programme) held in Malé (Maldives) on 22 April 98, all South Asian Governments have approved a Declaration on Control and Prevention of Air Pollution. This declaration is the end result of a process started on the joint initiation of UNEP/EAP-AP based at Asian Institute of Technology, Bangkok, SACEP and the Stockholm Environment Institute. On 20 March 1998, representatives of South Asian Governments, including India, Pakistan, Bangladesh, Nepal, Sri Lanka, Bhutan and Maldives met for a policy dialogue meeting held at the Asian Institute of Technology (AIT), Bangkok, Thailand and agreed in principle to a draft South Asian Declaration on Control and Prevention of Air Pollution. The policy dialogue meeting was organized by the United Nations Environment Programme/Environment Assessment Programme for Asia and Pacific (UNEP/EAP-AP) based at AIT, and the Stockholm Environment Institute (SEI) based in Stockholm, Sweden as part of the Regional Air Pollution Program in Developing Countries, funded by the Swedish International Development Co-operation (Sida) and managed by SEI.

The draft declaration was put before the South Asian environmental ministers for the official declaration at the Seventh meeting of the Governing Council of South Asia Cooperative Environment Programme (SACEP) held on 22 April 1998 in Malé, the Republic of Maldives. The Governing Council meeting was inaugurated by His Excellency Mr. Maumoon Abdul Gayoom, President of the Republic of Maldives and attended by ministers and high level policy makers from South Asian environment ministries. It resulted in the approval of the Declaration on control and prevention of air pollution by South Asian Governments.

The ***aim of the Declaration*** *is to achieve intergovernmental cooperation to address the increasing threat of transboundary air pollution and consequential impacts due to concentrations of pollutant gases and acid deposition on human health, ecosystem function and corrosion of materials. Besides laying down the general principles of intergovernmental cooperation for air pollution abatement, the Declaration sets up an institutional framework linking scientific research and policy formulation. The Declaration also calls for the continuation of this process in stages, with mutual consultation, to draw up and implement national and regional action plans and protocols based on a fuller understanding of transboundary air pollution issues.*

As a result of the Declaration the ***major implications in the short-term*** *could be: (I) evolving of an institutional structure at national level both for of policy response and the technical requirements; (ii) strengthening of monitoring arrangements; (iii) baseline studies to assess and analyze the air pollution issue; and (iv)* ***development and/or adoption of national action plans****.*

In the ***long-term****, the Declaration could be one of the* ***central means for protecting the atmospheric environment in South Asia****. In the years to come it could serve as one more bridge between different political systems and as a factor of some stability in years of* *political change. It could lead to the development of international environmental law and also create the essential framework for controlling and reducing the damage to human health and the environment caused by localized and transboundary air pollution. It is a successful example of what can be achieved through intergovernmental cooperation.*

In addition to the Declaration, a ***follow up action plan*** *has also been agreed. Follow up activities will be implemented in three levels, National, Sub-regional and Regional. In addition to the baseline studies and national action plans, a network of researchers and policy makers will also be established at the national level. At the sub-regional level, national level activities will be aggregated through SACEP. Dissemination of tools, methodologies, and data will be done at the regional level through a regional resource center. The follow up program will be implemented by UNEP/EAP-AP in collaboration with SEI and SACEP and with Sida support.*

Malé Declaration on
Control and Prevention of Air Pollution and its Likely Transboundary Effects for South Asia

Recognizing the potential for increase in air pollution and consequential phenomena due to concentration of pollutant gases, acid rain or acid deposition as well as the impacts on the health of humans and other living organisms in all our countries due to man made and natural causes; and also

Recognizing the potential for increase in transboundary air pollution as a corollary of air pollution in each country; and

Realising that the potential for air pollution increase and its transboundary effects will accumulate in the absence of national measures to abate and prevent such potential; and

Reiterating in this context Principle 21 of the UN declaration on the Human Environment in 1972 which stated that States have, in accordance with the charter of the United Nations and the principle of international laws, the sovereign right to exploit their own resources pursuant to their own environmental policies, and the responsibility to ensure that activities within their jurisdiction or control do not cause damage to the environment of other states or of areas beyond the limits of national jurisdiction;

Keeping in mind that need for constant study and monitoring of the trends in air pollution with a view to understand the extent of our potential for damage to the environment and health in the member countries and taking consequential measures to strengthen and build capacity for such activities;

Stressing the need for development and economic growth that will help build up the quality of life and incomes of all the people of all the region, in particular the poorer sections of the population, having due regard to the need to have a clean and healthy environment;

Emphasising that air pollution issues have to be analysed and managed in the wider framework of human and sustainable development within each country and within the region; and

Drawing from the experience of co-operation in the region in matters like cultural exchange and also from the experience in other regions like Europe and sub-regions of Asia like ASEAN and East Asia.

We declare that countries of this region will initiate and/or carry forward programmes in each country to

1. Assess and analyse the origin and causes, nature, extent and effects of local and regional air pollution, using the in-house in identified institutions, universities, colleges etc., building up or enhancing capacities in them where required;
2. Develop and/or adopt strategies to prevent and minimise air pollution;
3. *Work in co-operation with each other to set up monitoring arrangements beginning with the study of sulphur and nitrogen and volatile organic compounds emissions, concentrations and deposition;*
4. Co-operate in building up standardised methodologies to monitor phenomena like acid depositions and analyse their impacts without prejudice to the national activities in such fields;

5. Take up the aforesaid programmes and training programmes which involves then transfer of financial resources and technology and work towards securing incremental assistance from bilateral and multilateral sources;
6. Encourage economic analysis that will help arriving at optimal results
7. Engage other key stakeholders for example industry, academic institutions, NGOs, communities and media etc. in the effort and activities.

We also declare that we shall constantly endeavor to improve national reporting systems and strengthen scientific and academic effort in the understanding and tackling of air pollution issues.

We further declare that we shall continue this process in stages with mutual consultation to draw up and implement national and regional action plans and protocols based on a fuller understanding of transboundary air pollution issues.

We declare that in pursuit of the above, we shall evolve, as appropriate, institutional structures at the national level, including networking, both for the purposes of policy and the technical requirements, and we shall use the good offices of regional, international bilateral and multilateral agencies in this, as appropriate.

The list of participating countries and their National Implementing agencies of Malé Declaration

S.No.	Participating Country	National Focal Point	National Implementing Agency
1	**Bangladesh**	Ministry of Environment & Forest, Bangladesh Secretariat, Dhaka	Department of Environment, Ministry of Environment and Forest E-16, Agargoan, Sher-e-Bangla Nagar, Dhaka-1207
2	**Bhutan**	National Environment Commission, P.O. Box: 466, Thimphu	National Environment Commission, P.O. Box: 466, Thimphu
3	**India**	Ministry of Environment and Forests, Parayavaran Bhavan, CGO Complex, Lodi Road New Delhi 110 003	Central Pollution Control Board, "Parivesh Bhawan'" East Arjun Nagar New Delhi – 110 032
4	**Iran**	Department of Environment 187, Ostad Nejatollahi Ave., P.O. Box: 1587-5181 Tehran 15875	Department of Enviornment 187, Ostad Nejatollahi Ave., P.O. Box: 1587-5181 Tehran 15875
5	**Maldives**	Ministry of Home Affair, Housing & Environment Huravee Building, Male'	Ministry of Home Affairs, Housing & Environment Huravee Building, Male'
6	**Nepal**	Ministry of Population & Environment Singh Durbar, Kathmandu	International Centre for Integrated Mountain Development P.O. Box: 3226, Kathmandu
7	**Pakistan**	Ministry of Environment, Local Govt. & Rural Development UBL Building, Jinnah Avenue, Ialamabad	Pakistan Environment Protection Agency 4th Floor, 44-E, Office Tower, Blue Area, Islamabad
8	**Sri Lanka**	Ministry of Forestry & Environment, Sampathpaya, Rajamalwatte, Battaramulla, Colombo	Central Environmental Authority 240/1, Vauxhall Street Colombo

INTRODUCTION

This present practical manual on ‘**Water Analysis**” has been prepared with a main focus on the Training programme on “ Wet Deposition Monitring” held at Central pollution Control Board, Delhi, India during August, 4-9, 2003 under the phase II of the ***Malé Declaratrion on Control and Prevention of Air Pollution and its Likely Transboundary Effects for South Asia.***

The parameters covered under this training programme are *p*H (electrometric method), Electrical Conductivity (electrometric method), Alkalinity (Titration method), Acidity (Titration method), Hardness (EDTA Titrimetric method), Calcium (EDTA Titrimetric method), Magnesium (EDTA Titrimetric cum calculation method), Sodium (Flame Photometric method), Potassium (Flame Photometric method), Chloride (Argentometric method), Sulphate(Turbidimetric method), Nitrite(Colorimetric method), Ammonia(Phenate colorimetric method) and Phosphate(Stannous chloride method). The methods described are based on **“**Standard Methods for examination of water and wastewater”, APHA (American Public Health Association), (1998): 20th Edition, Washington, D.C., USA. Each parameter is described with General discussion, principle, procedure and its Environmental-significance.

1 pH – VALUE

1.0 GENERAL

pH is the negative logarithm of hydrogen-ion concentration in moles per litre at a given temperature. The pH of natural water is controlled by the carbon dioxide/bicarbonate equilibrium and usually ranges from 4.0 to 9.0. The majority of waters are slightly basic due to the presence of bicarbonates and carbonates. pH affects the chemical and biological properties of liquids and hence is an important estimation; e.g. for controlling corrosion, and water and waste treatment processes. Electrometric method is the most commonly used method for the measurement of pH.

2.0 ELECTROMETRIC METHOD

PRINCIPLE

The pH is determined by measurement of the electromotive force of a cell comprising of an indicator electrodes, an electrode responsive to hydrogen ions (glass electrode) immersed in the test solution and a reference electrode (usually calomel electrode). Contact between the test solution and the reference electrode is achieved by means of a liquid junction, in the reference electrode. A difference of 1 pH unit produces a potential charge of 58.16 mv at 25^oC. The electromotive force is measured with a pH to read directly as pH value.

3.0 INTERFERENCES

The glass electrode is free from interference such a colour, turbidity, colloidal matter, oxidant reductants etc. In case salinity is high a sodium ion error at pH 10 and above has to be compensated. Temperature affects the potential at electrodes and the ionization in the sample. The first effect can be overcome by a temperatures compensation adjustment provided on the most of the instruments. The second effect is inherent in the sample and is taken into consideration by recording both temperature and pH of each sample.

4.0 APPARATUS

4.1 **pH Meter :** mains or battery operated model (for field measurement) with temperature compensation adjustment and reading to an accuracy of 0.1 pH units.

4.2 **Glass electrode:** This must be compatible with the pH meter used and should cover the entire pH-range with minimum sodium ion error.

4.3 **Reference electrode:** Calomel electrode filled with 3 M KCl is widely used.

5.0 REAGENTS

5.1 **Standard pH buffer solution:** This can be prepared from buffer tablets (pH 4.0, 7.0 and 9.1) which are commercially available. However, an analyst can prepare his own solutions by referring to standard text book.

5.2 **Potassium Chloride (KCl) Solution:** Dissolve 22.37 g KCl in 100ml of distilled water.

6.0 PROCEDURE

6.1 Rinse the electrodes with distilled water and dry it with a soft tissue paper.

6.2 Standardize the instrument with the electrode immersed in a buffer solution with a pH close to that of the water to be tested.

6.3 If manual temperature compensation is provided, set it to the temperature of the buffer.

6.4 Check the electrode response occasionally by measuring a second buffer solution of different pH.

6.5 Rinse with distilled water and dry with tissue paper after every measurement. The difference in reading for the standard buffers should not exceed 0.1.

6.6 Immerse the electrode in the sample.

6.7 Set the temperature control adjustment knob to the temperature of the sample. Take final reading when it becomes stable.

7.0 EXPRESSION OF RESULTS

pH value should be reported to the nearest 0.1 pH unit. The temperature of the sample at the time of pH measurement should be indicated.

8.0 PRECISION AND ACCURACY

The precision and accuracy attainable with a pH meter depends on the type and condition of the instrument. A precision of ± 0.02 pH unit and an accuracy of ± 0.05 pH unit can be achieved.

9.0 PRECAUTIONS

9.1 Before making any measurement rinse the electrode(s) with distilled water and dry it with the tissue paper.

9.2 Ensure adequate level of filling solution in the reference electrode.

9.3 Always keep the electrode in distilled water, never allow them to dry out.

9.4 Standardize the instrument in case of any doubts with the pH buffer closer to the pH of the test sample.

9.5 Adjust the temperature compensation knob before reading.

9.6 After immersing the electrode, wait for some time so as to stablize the system. Take the reading as soon as it becomes constant.

9.7 No chemical preservation of sample is permissible.

9.8 Remove oil and grease from sample by filtration.

10.0 REFERENCES

APHA (American Public Health Association), (1998) : Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, P. 4.86 - 4.91.

2. ELECTRICAL CONDUCTIVITY

1.0 GENERAL

Conductivity is a measure of the ability of a water sample to carry an electric current and it depends on the ionic strength of the water. This mainly depends on the type of ions, their total concentration, mobility and valence, and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds do not dissociate and hence generally do not conduct any current.

The determination of electrical conductivity is a rapid and convenient means of estimating the concentration of electrolytes. In waters containing mostly mineral salts (waters used for public supply and many other ground or surface waters) this will not be very different from that of the dissolved solids. Hence, in such samples conductivity can be used as a measure of dissolved solids.

For a particular sample one can have a factor to convert electrical conductivity to dissolved solids. This factor will vary from sample to sample. Thus, in some cases measuring the conductivity and converting it into the dissolved solids, can be used as a check for the quality of the effluent discharged or for monitoring the treatment plant. The factor usually varies from 0.55 to 0.9. The factor is multiplied by conductivity/ (umhos /cm) to obtain dissolved solids. Some other important applications of conductivity measurements are:

a) To check the purity of distilled and deionized water.

b) To check the variations in the dissolved mineral concentration of raw water or waste water samples quickly.

c) Determination of the amount of ionic reagent required for certain precipitation and neutralization reactions, the end point in such cases is determined by a sudden change in the slope of the conductivity curve.

d) An approximate estimation of the aliquots which may be taken for the chemical determination.

The standard unit of electrical conductivity is milliSiemen per meter (1mS/m = 10 µmho/cm).

Conductivity of some waters is as follows:

1) Fresh Distilled Water : 1 to 3 µmho/cm
2) River Water : 50 to 500 µmho/cm
3) Hard waters : 1000 to 3000 µmho/cm
4) Some Inorganic Industrial wastes : > 10,000 µmho/cm

Electrolytic conductivity increases with temperature at a rate of approximately 2% degree C. Thus, significant errors can result from inaccurate temperature measurement. It is desirable to make the conductivity measurements at 25^{o}C. No chemical preservation of samples is permissible.

2.0 APPARATUS

2.1 Conductivity Meter

Conductivity Cell – Platinium electrode type

2.2 Thermometer: Capable of reading to the nearest of 0.1^{o}C and covering the range 10 to 30^{o}C.

3.0 REAGENTS:

3.1 **Conductivity water** free from carbon dioxide having very low conductivity is used for the preparation of all the standard solutions. Redistilled water must be boiled just before use and allowed to cool. The conductivity of this water should be less than 1µ mhos/cm.

3.2 **Standard Potassium Chloride (0.01 N)** Dissolve 745.6 mg anhydrous KCl in conductivity water and make up to 1000 ml at 25^{o}C. This is the standard reference solution having specific conductance of 1412 µmhos/cm.

4.0 CALIBRATION

Calibrate the conductivity meter using Standard Potassium Chloride 0.01N which has a conductivity of 1412 µmhos/cm at 25^{o}C.

5.0 CONDUCTANCE OF POTASSIUM CHLORIDE SOLUTIONS AT 25 ^{O}C

Concentration (N)	**SPECIFIC CONDUCTANCE µmho/cm**
0.0001	14.94
0.001	147
0.01	1,412
0.1	12,980
1.0	111,900

6.0 PROCEDURE

Conductivity measurement: Rinse the cell with distilled water followed by portion of sample to be tested. Adjust the temperature of the sample to 25± 0.1^{o}C. Measure the conductivity of the sample and note the temperature.

7.0 EXPRESSION OF RESULTS

Express the results in µmhos/cm or in µs /cm. Round off the results to the nearest whole number.

10 µmhos/cm = 10µS/cm = 1mS/m

8.0 PRECISION AND ACCURACY

The precision and accuracy of measurement depends on the instrument used and accuracy with which cell constant is determined. The precision and accuracy of about ± 1-2% is expected with a satisfactory instrument and a good analyst.

9.0 PRECAUTIONS:

9.1 When electrodes are not being used always keep them in water.

9.2 Always record the temperature and apply temperature correction. Error in this may cause significant error in the results.

9.3 Always use conductivity water for preparing standards.

9.4 Conductivity measurements should be made on the spot or as soon as possible.

10.0 REFERENCES

APHA (American Public Health Association), (1998) : Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, p. 2.44 - 2.47.

3. ACIDITY

1.0 GENERAL

Acidity of water depends on its capacity to donate H^+ ions. Acidity in water is due to uncombined CO_2, mineral acids and salts of strong acids and weak bases. The acidity due to CO_2 has not been a problem from the public health point of view, but mineral acidity (due to inorganic acids) has adverse effect on public health. Also acidity, if present in water creates corrosion problems in supply pipes and containers. It is defined as the capacity of a solution to neutralize a standard alkali.

2.0 . PRINCIPLE

Acidity of water sample is determined by neutralizing it with strong alkali at a certain pH value using indicators. Mineral acidity can be calculated by neutralizing sample to pH 4.3. Carbon dioxide and HCO_3^- present in the sample can be completely neutralized by titration at pH 8.3. Acidity is reported as $CaCO_3$ mg/l. This method is applicable for determination of acidity in water and wastewater samples

3.0 INTERFERENCES

The main interferences are due to turbidity, colour and presence of ions of A1, Fe and residual chlorine. These should be removed before titration.

Methods for Determination of Acidity

There are two methods for determination of acidity:

A. Titrimetric method using indicators.

B. Potentiometric titration method using pH meter.

A. Titrimetric Method using Indicator

4.0 REAGENTS

4.1 **Sodium Hydroxide Stock Solution (0.2 N):** Dissolve 8.0 gm NaOH in freshly boiled and cooled distilled water and dilute to 1 litre.

4.2 **Standard Sodium Hydroxide (0.02 N):** Dilute 100 ml of stock NaOH (0.2 N) to 1 litre with freshly boiled and cooled distilled water.

4.3.1 **Phenolphthalein Indicator -** Dissolve 1 gm phenolphthalein powder in 100 ml ethyl alcohol and add 100 ml distilled water. Add 0.02 N NaOH drop-wise to obtain pink colour solution.

4.4 **Methyl Orange Indicator:** Dissolve 0.1 gm in 100 ml freshly boiled and cooled distilled water.

5.0 PROCEDURE

Remove residual chlorine interference, if present, by adding appropriate amount of sodium thiosulphate (0.1 N). Colour can be removed by fitting through activated carbon placing on filter paper and filtering the sample. Turbidity can be removed by centrifugation of sample.

(i) Take 100 ml sample in 250 ml conical flask.

(ii) Add 5 drops of methyl orange indicator. If pink colour appears, add 0.02 N NaOH drop-wise till solution becomes faint orange (pH 4.3) and note down the volume of 0.02 N NaOH consumed (x).

(iii) Add 5 drops of phenolphthalein indicator to the same solution and continue titration till faint pink colour appears (pH 8.3). Note the volume of 0.02 N NaOH consumed (y).

Calculation

1. Mineral Acidity or free Acidity = mg/l as $CaCO_3$

$$\frac{(x) \times N \times 50{,}000}{\text{Volume of sample (ml)}}$$

2. Total Acidity mg/l as $CaCO_3$ =

$$\frac{(y) \times N \times 50{,}000}{\text{Volume of sample (ml)}}$$

Where,

(x) = ml of NaOH required for titration using methyl orange indicator

(y) = ml of NaOH required for titration with methyl orange and phenolphthalein indicator.

N = Normality of NaOH taken for titration.

Total acidity can also be determined by using phenolphthalein indicator to the original sample & by titrating with 0.02 N NaOH. Bromocresol green indicator can also be used in place of methyl orange.

B. Potentiometric Method using pH Meter

(i) Take 100 ml sample in a beaker and put it on a magnetic stirrer.
(ii) Dip pH electrode in the sample after calibration of pH meter.
(iii) Titrate with 0.02 N NaOH up to the pH of 4.3 and 8.3.
(iv) Calculate Acidity as above.

Result should be reported as Acidity mg/l as $CaCO_3$.

6.0 REFERENCE

APHA (American Public Health Association), (1998): Standard methods for the examination of water and wastewater, 20th Edition, Washington D.C. USA. p. 2.24 – 2.26

4. ALKALINITY

1.0 GENERAL

The alkalinity of water is a quantitative measure of the basic constituents of water and is defined as the capacity of the water to neutralize a strong acid at a designated pH. The alkalinity of natural waters is mainly due to the presence of salts of carbonates, bi-carbonates and hydroxide of calcium, magnesium, sodium and potassium. The borates, silicates & phosphates also contribute to some extent. Alkalinity value help in deciding chemical doses in water & wastewater treatment processes particularly in coagulation, softening and operational control of anaerobic digestion and suitability of water for irrigation purposes.

2.0 PRINCIPLE

Phenolphthalein and methyl orange are the indicators commonly used for alkalinity titrations. Alkalinity of a sample can be estimated by titrating with standard sulphuric acid. The alkalinity fraction equivalent to the amount of acid required to lower the pH of the 8.3 is called phenolphthalein alkalinity and the amount of acid required to lower pH to 4.5 from 8.3 is called methyl orange alkalinity. The sum of both phenolphthalein and methyl orange alkalinity is called total alkalinity.

Alkalinity value helps in deciding the doses of chemicals in water and waste water treatment process, particularly in coagulation, softening, operational control of anaerobic digestion and checking suitability of water for irrigation.

3.0 INTERFERENCE

The interferences are primarily due to residual chlorine, turbidity, colour etc. Residual chlorine can be removed by adding thio-sulphate. Potentiometric titration is recommended for coloured & turbid samples.

4.0 METHOD FOR DETERMINATION

There are two methods for determination of alkalinity :

A. Titrimetric Method Using Indicator
B. Potentiometric Method

5.0 REAGENTS

5.1 **Standard Sodium Carbonate Solution (0.05 N):** Dry approximately 5 gm of Na_2Co_3 (AR grade) at 250°C for 4 hours and then cool in a desiccator for 20 minutes. Weigh approx. 2.5 gm and note the correct weight (A). Then dissolve this Na_2CO_3 in 1 litre of distilled water. Prepare fresh solution every week.

5.2 **Standard Sulphuric or Hydrochloric Acid (0.02 N):** Dilute 200 ml of 0.1 N H_2SO_4 or HCL (prepared from 1N acid) to 1 litre with distilled water.

H_2SO_4 (1N) - Dilute 28 ml of concentrated acid to 1 litre with distilled water.

HCL (1N) - Dilute 83 ml of concentrated acid to 1 litre with distilled water.

5.3 **Standardization of Acid:** Take 40 ml of Na_2Co_3 solution in a beaker and add 60 ml distilled water. Add acid solution (approx. 0.1N) drop-wise to pH-5 using pH meter. Rinse electrode with distilled water before and after use each time. Boil the mixture for approx. 5 min. covering with a watch glass. Then cool to room temperature, rinse watch glass with distilled water and complete titration to pH inflection point.

5.4 Calculation

$$\text{Normality (N)} = \frac{A \times B}{53.00 \times C}$$

A - Exact weight of Na_2CO_3 taken for 1 litre of solution
B - ml of Na_2CO_3 taken for titration
C - ml of Acid used

1 ml of 0.1 N Acid = 5 mg $CaCO_3$
OR
1 ml of 0.02 N Acid = 1 mg $CaCO_3$

5.6 **Phenolphthalein Indicator Solution (pH 8.3)** - Dissolve 1 gm phenolphthalein in 100 ml 95% ethylalcohol or isopropyl alcohol and 10 0ml distilled water.

5.7 **Methyl orange Indicator Solution (pH-4.5) -** Dissolve 0.5 gm methyl-orange powder in distilled water and dilute to 1 litre with distilled water.

5.8 **Metacresol Purple Indicator Solution (pH-8.3) -** Dissolve 0.1 gm of metacresol purple in 100 ml distilled water.

5.9 **Bromocresol Green Indicator Solution (pH-4.5) -** Dissolve 0.1 gm of bromocresol green sodium salt in 100 ml distilled water.

5.10 **Sodium Thio-sulphate 0.1 N -** Dissolve 24.82 gm $Na_2S_2O_3$ 5H2O in 1 litre of distilled water.

6.0 PROCEDURE

6.1 Titrimetric Method

(i) Take 100 ml sample or an aliquot diluted to 100 ml in a conical flask of 300 ml capacity.

(ii) Add 1 ml of 0.1 N Na2 CO3 per mg of residual chlorine, if present.

(iii) Add 5 drops of phenolphthalein indicator if pink colour appears titrate with 0.02N H2SO4 or HCL to the colourless end point. (pH-8.3). Note down the volume of acid consumed. (A).

(iv) Add 5 drops of methyl-orange indicator to the above solution, if yellow colour appears continue titration with acid till pink end point (pH-4.5). Note the volume of acid consumed (B).

Note : *If, pink colour does not appear on addition of phenolphthalein indicator phenolphthalein Alkalinity is absent and continue as (iv).*

6.2 Potentiometric Method

(i) Use calibrated pH meter for pH measurement.
(ii) Take 100 ml sample in a beaker.

(iii) Put the beaker on a magnetic stirrer below the tip of burette filled with 0.02 N H_2SO_4 or HCL and dipping the pH electrode in the sample.

(iv) Put on magnetic stirrer and pH meter and start adding drop-wise 0.02 N acid up to pH 8.3 (if pH is above 8.3). Note down the volume of acid consumed (A).

(v) Continue titration as above till pH is reached at 4.5 ± 0.2 and note down the volume (B). At inflection point, pH changes suddenly.

7.0 CALCULATION

- Phenolphthalein Alkalinity in mg/l as $CaCO_3$ $= \dfrac{A \times 1000}{\text{Volume}}$

- Methyl-orange Alkalinity or Total Alkalinity in mg/l as $CaCO_3$ $= \dfrac{B \times 1000}{\text{Volume}}$

A = ml standard acid used for pH 8.3 or phenolphthalein indicator.
B = ml standard acid used for pH 4.5 or methyl-orange indicator.

Alkalinity Relationships

Results of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Alkalinity as $CaCO_3$
P = O	0	0	T
P < ½ T	0	2P	T-2P
P = ½ T	0	2P	0
P > ½ T	2P-T	2(T-P)	0
P = T	T	0	0

P = Phenolphthalein Alkalinity, T = Total Alkalinity

8.0 EXPRESSION OF RESULTS

Express the result in mg/l as $CaCO_3$

9.0 PRECAUTIONS

9.1 Do not dilute, concentrate or alter the sample in any way. As far as possible avoid filtration

9.2 Use only carbon dioxide free distilled water for all purposes such as preparation of reagents etc.

9.3 If possible titration is to be carried out on the spot . If not, the sampling bottle should be filled completely and the alkalinity is determined in shortest possible time , in any case, not latter than 24 hrs.

9.4 Use magnetic stirrer for stirrer purpose

9.5 Adjust the volume of sample and concentrations of the titrant such that the volume of titrant required is appropriate i.e. neither too low or too high.

10.0 REFERENCE

APHA (American Public Health Association), (1998): Standard methods for the examination of water and wastewater, 20th Edition, Washington D.C. USA. p.p. 2.26 –2.29

5. HARDNESS

1.0 GENERAL

Hardness in water is mainly due to calcium and magnesium ions. Though some other polyvalent ions such as aluminium, iron, manganese, strontium and zinc also contribute to hardness. In natural waters, it is defined as sum of the calcium and magnesium ions expressed as calcium carbonate. The degree of hardness of drinking water has been classified in terms of the equivalent $CaCO_3$ concentration as follows:

Soft	0	- 60mg/l
Medium	60	- 120 mg/l
Hard	120	- 180 mg/l
Very Hard	> 180 mg/l	

Hardness in water poses problem of scale formation in boilers. It is also objectionable for laundry and domestic purposes since it consumes a larger amount of soap.

Hardness may range from zero to hundreds of milligrams per litre in terms of calcium carbonate, depending on the source of water. 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, all hardness is carbonate hardness and noncarbonate hardness is absent.

2.0 PRINCIPLE

At a pH 10 ± 1 EDTA forms a soluble chelated complex with calcium and magnesium. Calcium and complexed magnesium ions also form a less stable complex with Eriochrome Black T indicator or calmagite. Thus, when EDTA is added to a flask, metal-indicator complex breaks to form a more stable metal-EDTA complex and when all the metal is complexed to EDTA indicator shows a sharp change in colour from wine red to blue. Magnesium ion must be present to yield a satisfactory end point in the titration. A small amount of complexometrically neutral magnesium salt of EDTA is therefore added to the buffer. Thus, this step automatically introduces sufficient magnesium and at the same time obviates a blank correction.

3.0 INTERFERENCES

Some metal ions interfere in the end point detection which can be overcome by addition of inhibitors. Usually this interference is unlikely in surface waters.

4.0 REAGENTS

4.1 Buffer Solution

4.1.1 Dissolve 16.98 ammonium chloride (NH_4Cl) in 143 ml conc. ammonium hydroxide, NH_4OH, add 1.25 g of magnesium salt of EDTA, and dilute to 250 ml with distilled water.

4.1.2 If the magnesium salt of EDTA is not available, dissolve 1.79 disodium salt of ethylenediamine tetracetic acid dihydrate (analytical reagent grade) and 780 mg Mg SO_4. $7H_2O$ or 644 mg $MgCl_2$ $6H_2O$ in 50 ml distilled water. Add this solution to 16.9 g NH_4Cl and 413 ml conc. NH_4OH with mixing and dilute to 250ml with distilled water.

Store the solution 1 or 2 in a plastic container. Do not store more than a month’s supply in a frequently opened container.

4.2 Indicator

4.2.1 Erichrome Black –T (EBT):
Mix 0.5 g of indicator with 100 g of solid sodium chloride. Grind together in a mortar to obtain a homogenious mixture of 40-50 mesh size. Use about 0.2 to 0.4 g of the ground mixture for each titration.

4.2.2 Calmagite

1 – (1 –hydroxy – 4 methyl, 2 phenylazo) 2 napthol – 4 sulphonic acid is a dye produce same colour change as EBT when titrated for hardness estimation. It has a more sharp end point. Dissolve 0.1 g calmagite in 100 ml distilled water. Use 1 ml indicator per 100 ml sample to be titrated.

4.2.3 Standard EDTA titrant 0.01 M:
Dissolve 3.72 3 g AR Grade disodium salt EDTA in distilled water, and dilute to 1 litre, Standardize against standard calcium. This solution is about 1.00 mg Ca CO_3/ml.

4.2.4. Standard calcium solution 0.1 M:
Weigh 1.000 g anhydrous calcium carbonate into a 500ml conical flask. Place a funnel on the neck of the flask and add slowly 1+1 HCl until all the $CaCO_3$ has dissolved. Add 200ml distilled water and boil for a few minutes to expel out all 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. Transfer quantitatively to a 1 litre volumetric flask and make up the volume to the mark. This standard solution is 1 ml= 1.00 mg $CaCO_3$.

5.0 PROCEDURE

Take 100 ml sample, or smaller appropriate portion diluted to 100 ml containing hardness of about 10 to 20 mg, in a porcelelain dish or conical flask. Add 2 ml buffer solution followed by about 0.2-0.4 g of solid indicator. Titrate immediately but slowly with continuous stirring, until the last reddish tinge disappears and blue colour is observed. Reagent blank may be used for comparison. Reagent blank is titrated in a similar way as for the sample.

Standardize EDTA titrant with calcium standard in a similar way as described for the sample.

6.0 CALCULATION

$$\text{Hardness as mg/l } CaCO_3 = \frac{(V_1-V_2) \times A \times 1000}{\text{ml sample}}$$

Where

V_1 is the volume of EDTA required for sample

V_2 is the volume of EDTA required for reagent blank

A is the mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant

7.0 EXPRESSIONS OF RESULTS

Hardness is expressed as mg/l $CaCO_3$. Round off the results to nearest whole number.

8.0 PRECISION AND ACCURACY:

The Precision and accuracy depends on hardness concentration. When the concentration is more than 25 mg/l, precision and accuracy of about ± 2 to 4% can be achieved.

9.0 PRECAUTIONS

9.1 Carry out the titration within 5 minutes to minimize the tendency towards $CaCO_3$ precipitation.

9.2 The final volume of sample and blank should be kept constant (Usually 100 ml).

9.3 Use deionized or double distilled water for dilutions, blank estimation, etc.

9.4 Use reagent blank for colour comparison.

9.5 Add same quantity of indicator for sample and blank.

9.6 Adjust volume of sample such that hardness is in range 5 to 20 mg.

10.0 REFERENCE

APHA (American Public Health Association), (1998) : Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, P. 2.36 – 2.39.

6. CALCIUM

1.0 GENERAL

Calcium is necessary in plant and animal nutrition and is an essential component of bones, shells, and plant structures. The presence of calcium in water supplies results from passage over deposits of limestone, dolomite, gypsum, and gypsiferous shale. Small concentrations of calcium carbonate combat corrosion of metal pipes by laying down a protective coating. Because precipitation of calcite in pipes and in heat exchangers can cause damage, the amount of calcium in domestic and industrial waters is often controlled by water softening (e.g., ion exchange, reverse osmosis). Calcium contributes to the total hardness of water. The most common forms of calcium are calcium carbonate (calcite) and calcium-magnesium carbonate (dolomite). Calcium compounds are widely used in pharmaceuticals, photography, lime, de-icing salts, pigments, fertilizers, and plasters. Calcium carbonate solubility is controlled by pH and dissolved CO_2. The CO_2, HCO_3^-, and CO_3^{2-} equilibrium is the major buffering mechanism in fresh waters. Hardness is based on the concentration of calcium and magnesium salts, and is often used as a measure of potable water quality.

2.0 PRINCIPLE

The atomic absorption spectrophotometer method is the most accurate method available for the calcium determination. But the EDTA titrimetric method also gives good results for routine applications. Due to simplicity and rapidity of the EDTA method it has become first choice of the analyst. When EDTA (ethlenediaminetetraacetic acid or its 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. Several indicators give a color change when all of the calcium has been complexed by the EDTA at a pH of 12 to 13.

3.0 INTERFERENCES

Under conditions of this test, the following concentrations of ions cause no interference with the calcium hardness determination: Cu^{2+}, 2mg/L; Fe^{2+}, 20mg/L; Fe^{3+} , 20mg/L; Mn^{2+}, 10mg/L; Zn^{2+}, 5mg/L; Pb^{2+}, 5mg/L; Al^{3+}, 5mg/L and Sn^{4+}, 5mg/L. Orthophosphate precipitates calcium at the pH of the test. Strontium and barium give a positive interference and alkalinity in excess of 300 mg/L may cause in indistinct end point in hard waters.

4.0 REAGENTS

4.1 Standard EDTA Solution (0.01 M): Dissolve 3.723 g AR grade Ethylene diamine tetra acetic acid (EDTA) di-sodium salt $Na_2C_{10}H_{12}O_8N_2$. $2H_2O$ in distilled water and dilute of 1 litre. Standardize it against standard calcium solution. Standard EDTA titration 0.01 M is equivalent to 400.8 ug calcium/ml.

4.2 Sodium Hydroxide NaOH (1N) : Dissolve 40g sodium hydroxide in distilled water and make up the volume to 1 litre. Store in polythene bottle.

4.3 Indicators

4.3.1 Murexide (Ammonium Purpurate) : Changes colour from pink to purple at the end point. Prepare by mixing 200 mg dye in 100 g solid Sodium chloride, grind it to 40-50 mesh. This indicator is unstable in alkaline condition.

4.3.2 **Eriochrome Blue Black R indicator:** Mix 200 mg dye with 100 g NaCl and grind it to 40-50 mesh, 0.2 to 0.4 g of the mixture is required for each titration. During the course of titration, the colour changes from red through purple bluish purple to a pure blue without any trace of reddish or purple tinge. pH of the sample may be raised to 14 by adding 8 N NaOH in order to get a sharper colour change.

4.4 **Standard Calcium Solution:** Weigh 1.000 g anhydrous $CaCO_3$ (Calcium carbonate) powder (primary standard) with low heavy metals, alkalis and magnesium into a 500 ml Erlenmeyer flask. Place a funnel in the neck of the flask and add a little at a time (1+1) HCl until the $CaCO_3$ dissolves. Add 200 ml distilled water and boil for few minutes to expel CO_2. Cool and add few drops of methyl red indicator, adjust the colour to intermediate orange colour by adding 3 N NH_4OH or 1+1 HCl as required. Transfer the solution to volumetric flask and dilute to 1000 ml. Discard the solution if any precipitate or growth is found.

1 ml $CaCO_3$ solution is equivalent to 1 mg $CaCO_3$.

5.0 PROCEDURE

Take 100 ml or smaller portion diluted to 100 ml so that calcium content is about 10 to 20 mg. Add 5ml NaOH solution to produce a pH of 12 to 13. Stir and add about 0.2 –0.4g of indicator mixture. Because of the high pH required, titrate immediately after adding alkali and indicator. Add EDTA titrant slowly with continous stirring to the proper end point.

Carry out a reagent blank using 100 ml distilled water under identical conditions.

Standardize EDTA titrant with calcium standard following the same method as described for the samples.

6.0 CALCULATION

$$\text{Calcium hardness as mg CaCO/l} = \frac{(V_1 - V_2) \times A \times 1000}{\text{ml sample}}$$

Where,

V_1 is the volume of EDTA required for sample.
V_2 is the volume of EDTA required for reagent blank.
A is the mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant.

Calcium as Ca^{++} (mg/l) = Calcium hardness as $CaCO_3$ mg/l X 0.4

7.0 EXPRESSION OF RESULTS

Results are expressed as mg/1 of $CaCO_3$. Round off the result to the nearest whole number.

8.0 PRECISION AND ACCURACY

The precision and accuracy of about + 2 to 4% is expected from a good analyst, when the concentration is more than 25 mg/l. Procision and accuracy also depends on the quantity of calcium present.

9.0 PRECAUTIONS

9.1 Titrate immediately after adding the indicator because it is unstable under alkaline conditions.
9.2 For recognising end point use a colour comparision blank prepared under identical conditions.
9.3 The final volume for sample and blank should be kept constant.
9.4 Use deionized distilled water for reagent preparations and dilution, if necessary.
9.5 Add same quantity of indicator to sample and blank, so that the colour comparison is better.

10.0 REFERENCE

APHA (American Public Health Association), (1998) : Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, p. 3.63 - 3.65.

7. MAGNESIUM

1.0 GENERAL

Similar to calcium, magnesium is also a common constituent of natural water. It is one of the important contributors to the hardness of water. Magnesium concentration in water may vary from zero to several hundred milligrams per litre depending upon the source of water. Concentrations greater than 125 mg/l can exert a cathartic and diuretic action. Chemical softening or ion exchange reduces the magnesium and associated hardness to acceptable levels.

2.0 PRINCIPLE

While measuring total hardness, calcium and magnesium ions react with EDTA to form soluble complexes and completion of reaction is indicated by the colour change of a suitable indicator. By substracting the value of calcium hardness from total hardness, magnesium hardness can be measured. Magnesium as Mg^{++} can be calculated by multiplying magnesium hardness with 0.243. This method is applicable for determination of magnesium in water and wastewater samples.

3.0 INTERFERENCE

Suspended or colloidal organic matter may interfere with end point of the titration.

4.0 REAGENTS

4.1 Total Hardness as $CaCO_3$

(Refer method on Determination of Hardness)

4.2 Calcium Hardness as $CaCO_3$

(Refer method on Determination of Calcium hardness)

5.0 PROCEDURE

(Refer method on Determination of Hardness and Calcium hardness)

6.0 CALCULATION

Magnesium as equivalent $CaCO_3$ may easily be estimated as the difference between total hardness and calcium hardness as $CaCO_3$:

Magnesium as Mg^{++} mg/l =

$$(\text{Total Hardness as mg } CaCO_3/l - \text{Calcium Hardness as mg } CaCO_3/l) \times 0.243$$

7.0 EXPRESSION OF RRESULTS

Results are expressed **as Mg^{++} (mg/l)**

Report to the nearest whole number

8.0 PRECAUTIONS

Conduct titrations at or near normal room temperature.

9.0 REFERENCE

APHA (American Public Health Association), (1998): Standard Methods for examination of water and wastewater, 20th Edition, Washington, D.C., USA. p. 3.82-3.83.

8. SODIUM

1.0 GENERAL

Sodium is present in most natural waters from negligible to appreciable concentrations. The sea water contains nearly 12,000 mg/l of sodium ions. Generally the groundwater contains more sodium ions when compare to natural surface water. High sodium content in irrigation water leads to Sodicity problem in soil thus affects crop growth.

2.0 PRINCIPLE

Trace amounts of Sodium can be determined by flame emission photometry. Sample is aspirated into a gas flame under carefully controlled, reproducible excitation conditions. The light intensity is measured and is approximately proportional to the concentration of the element. The calibration curve may be linear but has a tendency to level off or even reverse at higher concentrations to minimise this effect operate the instrument at the lowest practical concentration range. Work in the linear to near linear range. Minimum detectable concentration is approximately 5 µg/l. This method is applicable for determination of sodium in water and wastewater samples.

3.0 INTERFERENCE

Potassium and calcium interfere with sodium determination. It can be eliminated by the internal standard method, if the potassium sodium ration is $\geq$ 5:1 and the calcium sodium ratio is $\geq$ 10:1. When these ratio are exceed, determine calcium and potassium concentrations and matrix-match sodium calibration standards by addition of approximately equivalent concentrations of interfering ions.

3.1 Instrument Operation

Follow manufacturer's instruction manual for selecting the appropriate sensitivity, fuel and oxidant gas pressure, and the steps of warm-up, correcting for interferences and flame background, rinsing of burner, ignition flame etc.

3.2 Equipment and Auxiliaries

(a) Flame Photometer

(b) **Glassware:** Rinse all glassware with 1 + 15 HNO_3 followed by several portions of de-ionised distilled water.

4.0 REAGENTS

(a) **De-ionised distilled water**: Use de-ionised distilled water to prepare all the reagents, calibration standards and dilution water.

(b) **Stock Sodium Solution**: Dissolve 2.542 g NaCl dried at 140°C to constant weight and dilute to 1000 ml with de-ionised distilled water ; 1.00 ml = 1.00 mg Na.

(c) **Intermediate Sodium Solution**: Dilute 10.00 ml stock sodium solution with water to 100 ml; 1 ml = 0.10 mg Na. Use this solution to prepare calibration curve in sodium range of 1 to 100 mg/l.

(d) **Standard Sodium Solution**: Dilute 10 ml intermediate sodium solution with water to 100 ml, 1.0 ml = 0.01mg Na. Use this solution to prepare calibration curve in sodium range of 0.1 to 10 mg/l.

Note : *To minimise sodium contamination, store all solutions in plastic bottles to reduce the amount of dry element that may be picked up from the bottle walls when solution is poured. Shake each container vigorously to wash accumulated salts from walls before pouring solution.*

5.0 PROCEDURE

(a) Pre-treatment of polluted and wastewater samples : Samples containing particulates or organic materials generally require pre-treatment before analysis. Colourless, transparent samples having a turbidity < 1 NTU, no odour may be analysed directly. Digest all other samples before analysis.

(b) For digestion, mix the sample and take the appropriate volume (50 - 100 ml) in a conical flask, add 5 ml concentrate, HNO_3 and few boiling chips. Heat the sample on a hot plate at 70-80°C until the lowest volume is reached. Continue heating and adding small volumes of concentrate HNO_3 until a clear solution is obtained. Filter the digested solution and dilute the sample with distilled water to the original volume.

5.1 Direct Reading Measurement

Calibration: Prepare a blank and sodium calibration standards in stepped amounts in any of the following applicable ranges: 0-1.0, 0-10 or 0-100 mg/l. Aspirate calibration standards and samples enough times to secure a reliable average reading for each. Construct a calibration curve from sodium standards.

5.2 Measurement

Determine sodium concentration of samples from calibration curve. Where a large number of samples must be run routinely, the calibration curve provides sufficient accuracy.

6.0 CALCULATION

For direct reference to the calibration curve:

Sodium (mg /L) = (mg Na/L in portion) X D (Dilution Factor)

7.0 REFERENCE

APHA (American Public Health Association), (1998): Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, P. 4.139 - 4.146.

9. POTASSIUM

1.0 GENERAL

Potassium ranks seventh among the elements in the order of abundance. Potassium is an essential element, but in excessive amounts it acts as a cathartic. It occurs in ground waters as a result of mineral dissolution from decomposing plant material and from agriculture run off its concentration. It is determined by flame photometric method.

2.0 PRINCIPLE

Trace amounts potassium can be determined in direct reading type of flame photometer. The sample is aspirated into a gas mixture flame and excitation is carried out under carefully controlled and reproducible conditions. The intensity of light is measured by a photo tube. The intensity of light is approximately proportional to the concentration of the element. The calibration curve may be linear but has a tendency to level off at higher concentration. Minimum Detectable Concentration of approximately 0.1 mg/L can be determined by this method. This method is applicable for determination of potassium in water and wastewater samples.

3.0 INTERFERENCES

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

4.0 APPARATUS

a) **Flame Photometer.**

b) **Glassware:** Rinse all glassware with 1:15 HNO_3 followed by several portions of de-ionised distilled water.

4.1 Instrument Operation : Follow the manufacturer's instruction manual for selecting the appropriate sensitivity, fuel and oxidant gas pressure, and the steps of warm up, correcting for interferences and flame background, rinsing of burner ignition flame etc.

5.0 REAGENTS

a) **De-ionised distilled water**: Use for preparing all reagents and calibration standards and as dilution water.

b) **Stock Potassium Solution** : Dissolve 1.907 g KCl dried at 110°C and dilute to 1000 ml with water, 1 ml = 1.00 mg K

c) **Intermediate Potassium Solution**: Dilute 10.0 ml Stock potassium solution with water to 100 ml. 1.00 ml = 0.100 mg K. Use this solution to prepare calibration curve in potassium range of 1 to 10 mg/L.

d) **Standard Potassium Solution**: Dilute 10.0 ml intermediate potassium solution with water to 100 ml; 1.00 ml = 0.01 mg K. Use this solution to prepare calibration curve in potassium range of 0.1 to 1. mg/L.

Note : To minimise potassium pick up, store all solutions in plastic bottles, shake each container thoroughly to dissolve accumulated salts from walls before pouring.

6.0 PROCEDURE

Pre-treatment of polluted and wastewater samples:

Samples containing particulate or organic materials generally require pre-treatment before analysis. Colourless, transparent samples having turbidity < 1 NTU, no odour may be analysed directly.

Digestion: If the sample is turbid, mix the sample and take the appropriate volume (50-100 ml) in a conical flask, add 5 ml conc. HNO_3 and few boiling chips. Heat the sample on a hot plate at 70-80^oC until the lowest volume is reached. Continue heating and adding small volumes of conc. HNO_3 until a clear solution is obtained. Filter the digested solution and dilute to the original volume with distilled water.

7.0 INSTRUMENT OPERATION

Follow manufacturer's instruction manual for selecting proper photocell, wave length, adjusting grit width and sensitivity, appropriate fuel and air or oxygen pressure and the steps for warm up, correcting for interference and flame background, rinsing of burner, igniting sample and measuring emission intensity.

7.1 Direct Reading Measurement

Calibration: Prepare a blank and potassium calibration standards in stepped amounts in any of the following applicable ranges; 0-1.0, 0-10 or 0-100 mg/l K. Aspirate calibration standard and samples enough time to secure a reliable average reading for each standard. Construct a calibration curve from potassium standards.

7.2 Measurement

Determine potassium concentration of samples from calibration cure. Where a large number of samples must be run routinely, the calibration curve provides sufficient accuracy.

8.0 CALCULATIONS

(a) For direct reference to the calibration curve

Potassium (mg//L) = mg K/L in portion X D (Dilution factor)

9.0 REFERENCE

APHA (American Public Health Association), (1998): Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, P. 4.139 - 4.146.

10. CHLORIDE

1.0 GENERAL

Chloride is one of the major inorganic anions in water and wastewater. A high concentration occurs in waters from chloride-containing geological formations. Otherwise, a high chloride content may indicate pollution by sewage or some industrial wastes or an instruction of sea water or other saline water. The salty taste produced by chloride depends on the chemical composition of the water. Some waters containing 250 mg Cl^-/L may have a detectable salty taste if the cation is Sodium, on the other hand, the typical salty taste may be absent in waters containing 1000 mg/l of chloride when the predominant cations are calcium and magnesium. Although Chlorides are not harmful, concentration beyond 250 mg/l impart a peculiar tests to water rendering it unacceptable from aesthetic point of view for drinking purpose. A high chloride concentration harms metallic pipes and structures, as well as agricultural plants.

2.0 ARGENTOMETRIC METHOD

PRINCIPLE

Two methods, both titrimetric-argentometric and mercurimetric method are described. Wherever colour of the sample interference with the chromate end point in argentometric method, the other method may be used. The argentometric method is suitable for relatively clear waters when 0.15 to 10 mg chloride are present in the portion titrated. The end point of mercurimetric method is comparatively easier to detect. Chloride is determined in a neutral or slightly alkaline solution by titration with standard silver nitrate, using potassium chromate as indicator. Silver Chloride is precipitated quantitatively before red silver chromate is formed.

3.0 INTERFERENCES

Substances in amounts normally found in potable waters do not interfere. Bromide, iodide and cyanide are measured as equivalent to chloride ion. Sulfide, thiosulfate, and sulfite interfere. They may be oxidized to non-interferring substances by pretreatment with hydrogen peroxide.

4.0 REAGENTS

Silver Nitrate Standard Solution 0.0141N: Dissolve 2.395 g silver nitrate in distilled water and dilute it to 1,000 ml. Store in brown glass bottle. 1.00 ml = 500 µgCl^- Standardization titration with standard sodium chloride must be carried out without any dilution.

Standard Sodium Chloride, 0.0141N: Dissolve 824.0 mg NaCl (dried at 140^{o}C) in distilled water and dilute to 1,000 ml. 1.00 ml= 500 µgCl^-

Potassium Chromate Indicator Solution: Dissolve 50 g $K_2 CrO_4$ in a little distilled water. Add silver nitrate solution dropwise until definite red precipitation starts. Let it stand for 12 hrs, filter and dilute to 1 litre with distilled water.

Note: Use chloride-free i.e. redistilled or deionized distilled water for the preparation of all above reagents. Same water should be used for the sample dilutions also (wherever required). Avoid dilutions as far as possible or apply blank correction.

5.0 PROCEDURE

Take 100 ml sample or a suitable portion diluted to 100 ml into a porcelain dish, or conical flask or breaker on a white surface.

Titrate samples in the pH range 7 to 10 directly. Adjust samples not in this range with H_2SO_4 or NaOH solution. Add 1 ml potassium chromate solution and titrate with silver nitrate solution with constant stirring to a pinkish yellow end point. Be consistent in end point recognition. It is suggested to use reagent blank as a comparator. If the volume of the titrant exceeds 25 ml then it is better to repeat the method with smaller portion of the sample.

Standardize the silver nitrate titrant with standard sodium chloride. Carry out the blank determination to account for the chloride present in any of the reagents and for the solubility of silver chromate. A blank of 0.2 to 0.4 ml is usual for the method.

6.0 CALCULATION

$$\text{Chlorides as } Cl^- \text{ mg/L} = \frac{(V_1 - V_2) \times N \times 35.45 \times 1000}{\text{ml Sample}}$$

Where,

V_1 = Volume of silver nitrate required for sample, in ml

V_2 = Volume of silver nitrate required for reagent blank, in ml

N = Normality of Silver Nitrate.

7.0 EXPRESSION OF RESULTS

Results are expressed in mg/l Cl^-

The results should be rounded off :to first decimal for values upto 20 mg/L and to whole number for above 20 mg/L.

8.0 PRECISION AND ACCURACY

The precision and accuracy of about ± 2% to 4% is expected from a good analyst, except in the samples where chloride content is less than 50mg/l.

9.0 PRECAUTIONS

9.1 Use white opque background for titration.

9.2 Adjust the volume of sample such that titrant value is in the range 5-20 ml as far as possible.

9.3 For coloured samples use mercurimetric method.

9.4 Be consistent in end-point recognition. Reagent blank may be used for end point comparison.

9.5 Use Chloride free distilled water for the preparation of reagents as well as dilutions, if any.

10.0 REFERENCE

APHA (American Public Health Association), (1998) : Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, P. 4.66 - 4.69.

11. SULPHATE

1.0 GENERAL

Sulphate ion is one of the major anions occurring in natural waters. It occurs naturally in water as result of leaching from Gypsum and other common minerals. In addition, Sulphate may be added in several treatment processes. It is of importance in public water supplies because of its cathartic effect upon humans when it is present in excessive amounts i.e. more than 250 mg/l. The sulphate content of municipal water supplies is usually increased during clarification by alum. Sulphates contribute to the total solids content and the determination of sulphate is sometimes used to control the washing of turbine blades to free them from deposits.

2.0 PRINCIPLE

Sulphate (SO_4^{2-}) ions are precipitated in a hydrochloric acid medium with Barium Chloride ($BaCl_2$) so as to form a uniform suspension of $BaSO_4$. The absorbance of the $BaSO_4$ suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with standard curve. The turbidimetric method is more rapid and is especially applicable to waters with sulphate concentration up to 60 mg/l.

3.0 INTERFERENCE

Colour or suspended matter in large amounts will interfere. Suspended matter may be removed by filtration. If both are small in comparison to sulphate concentration, this interference is corrected by running blank in which $BaCl_2$ is eliminated.

Silica in excess of 500 mg/L will interfere and in water containing large quantities of organic material it may not be possible to precipitate $BaSO_4$ satisfactorily. The minimum detectable concentration is approximately 1 mg SO_4^{2-}/L.

4.0 APPARATUS

a) Magnetic Stirrer with stirring bars.
b) Spectrophotometer for use at 420 nm providing a light path of 2.5 to 100 nm.
c) Stopwatch
d) Measuring spoon. Capacity 0.2 to 0.3 ml.

5.0 REAGENTS

(a) **Conditioning Reagent**: Mix 50 ml glycerol with a solution containing 30 ml concentrated HCl, 300 ml distilled water, 100 ml 95% ethyl alcohol and 75 g. NaCl.

(b) **Barium Chloride**: Crystals, 20-30 mesh.

(c) **Stock Sulphate Solution**: Dissolve 1.4798 g. anhydrous Na_2SO_4 in distilled water and dilute to 1000 ml. 1 ml = 1 mg SO_4.

(d) **Standard Sulphate Solution**: Dilute 10 ml of stock solution to 100 ml with distilled water, 1 ml = 0.1 mg SO_4.

6.0 PROCEDURE

6.1 Calibration Curve

(a) Measure in 250 ml conical flask 10.0, 20.0, 30.0, 40.0, 50.0 ml of standard sulphate solution and dilute to 100 ml.

(b) Add 5.0 ml conditioning reagent and mix well using magnetic stirrer. The speed of stirring should be the same for both standards and samples.

(c) While stirring add about 0.5 g. $BaCl_2$ crystals and continue to stir exactly one minute.

(d) Immediately after one minute, pour some of the solution into the absorption cell and measure the optical density at 420 nm at 30 seconds intervals for four minutes taking the maximum turbidity which will normally be after a period of 2 minutes after completion of stirring.

(e) Carry out reagent blank using distilled water.

(f) Prepare a calibration curve for sulphate concentrated v/s absorbance.

6.2 Sample Measurement

(a) Measure in a 250 ml conical flask a suitable quantity of the sample and dilute to 100 ml and proceed from step (b) to (e) as for standards.

(b) From the calibration graph read the mg/l sulphate concentration equivalent to absorbance.

7.0 CALCULATIONS

SO_4 (mg/l) = Concentration of mg/l, obtained after comparison with calibration curve X D

Where ,

D = dilution factor.

Note : *If the sample is coloured or turbid, conduct a sample blank using the same amount of sample and conditioning reagent, without adding $BaCl_2$. Measure the absorbance and substract the value from absorbance of the $BaCl_2$ added sample and note down the concentration of sulphate.*

8.0 REFERENCE

APHA (American Public Health Association), (1998) : Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, P. 4.139 - 4.146.

12. NITRITE NITROGEN

1.0 GENERAL

The presence of nitrite in water indicates organic pollution. Biological decomposition of nitrogenous organic matter such as sewage and animal wastes contributes nitrite. The concentration of nitrite in drinking water rarely exceeds 0.1 mg/l. In excessive amount, it contributes to the illness known as methemoglobinemia in infants.

2.0 PRINCIPLE

Nitrite (NO_2^-) is determined through formation of a reddish purple azodye produced at pH 2 to 2.5 by coupling di-azotized Sulphanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride. The applicable range of the method for Spectrophotometric measurements is 10 to 1000 µg NO^-_2N/L. The colour system obeys beer's law up to 180 µg N/L with a 1 cm. light path. Higher NO_2^- concentrations can be determined by diluting the sample. The colour measurement is done at 543 nm. This method is applicable for determination of nitrite nitrogen in water and wastewater samples.

3.0 APPARATUS

a) Spectrophotometer for use at 543 nm.
b) Nessler Tubes - 50 ml with stopper.

4.0 REAGENTS

a) **Nitrite free water:** Use Nitrite free water for all the reagents

b) **Sulphanilamide reagent:** Dissolve 5 g sulphanilamide in a mixture of 50 ml concentrated HCl and 300 ml distilled water and make up to 500 ml.

c) **NED dihydrochloride reagent:** Dissolve 0.5 g of N-(1-naphthyl)-ethylenediamine dihydrocholride(NED dihydrochloride) in 500 ml distilled water.

d) **Stock Nitrite Solution:** Dissolve 1.232 g $NaNO_2$ in water and dilute to 1000 ml, 1.00 ml=250 µg N. Preserve with 1 ml $CHCl_3$.

e) **Intermediate Nitrite Solution:** Dilute 50 ml of stock nitrite solution to 250 ml, 1.0 ml = 50 µg N. Prepare freshly daily.

f) **Standard Nitrite Solution:** Dilute 10.00 ml intermediate NO_2^- solution to 1000 ml with water, 1.00 ml = 0.500 µg N. Prepare daily.

5.0 PROCEDURE

If sample contains suspended solids, filter through a 0.45 µm pore-diam membrane filter. If sample pH is not between 5 and 9 adjust to that range with 1 N HCl or NH_4OH as required. To 50.0 ml, add 1ml sulphanilamide reagent, 1ml of NED dihydrochloride) reagent and mix. Measure absorbance at 543 nm after 10 min but before 2 hr.

6.0 CALCULATION

Prepare a standard curve by plotting absorbance of standards against NO_2-N concentration. Compute sample concentration directly from curve.

7.0 REFERENCE

APHA (American Public Health Association), (1998) : Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA. pp. 4-112 – 4-114

13. AMMONICAL NITROGEN

1.0 GENERAL

Ammonical Nitrogen is very important parameter for fresh and wastewaters because it is the indicator, which shows the presence of nitrogenous matter. Ammonia is produced by the decomposition of nitrogenous matter, because all forms of nitrogen are inter-convertible. It also indicates the microbial activity in water, therefore, ammoniacal nitrogen should not be present in the drinking water. Certain level of ammoniacal nitrogen in water is toxic to fish and aquatic life. The different forms of ammonia (free or combined) depend on pH. Ammonia is liberated above pH 6. Hence, lowering the pH to 2.0 to by adding H2SO4 should immediately preserve sample.

2.0 PRINCIPLE

An intensely blue compound, indophenols, is formed by the reaction of ammonia, hypo chlorite, and phenol catalyzed by sodium nitroprusside. This method is applicable for determination of ammonical nitrogen in water and wastewater samples.

3.0 INTERFERENCES

Complexing Mg and Ca with citrate eliminates interference produced by precipitation of these ions at high pH. Remove interfering turbidity by distillation or filtration. H_2S removed by acidifying sample to pH 3 with HCl.

A. PHENATE METHOD

4.0 REAGENTS

4.1 **Phenol solution –** Mix 11.1 ml liquefied phenol ($\geq$ 89%) with 95% v/v ethyl alcohol to a final volume of 100 ml. Prepare weekly (Caution: wear gloves and eye protection while handling the phenol).

4.2 **Sodium Nitroprusside, 0.5% w/v -** Dissolve 0.5 g. Sodium Nitroprusside in 100 ml distilled water, store in a amber bottle for upto 1 month.

4.3 **Alkaline Citrate -** Dissolve 200 g trisodium citrate and 10 g sodium hydroxide in distilled water, dilute to 1000 ml.

4.4 **Sodium Hypo Chloride**, commercial solution, about 5%. Replace about every two months.

4.5 **Oxidizing solution –** Mix 100 ml alkaline citrate solution with 25 ml sodium hypo chloride. Prepare fresh daily.

4.6 **Stock ammonia solution -** Dissolve 3.819 g anhydrous NH_4Cl (dried at $100^{o}C$) in distilled water and dilute to 1000 ml. 1 ml = 1.00 mg NH_3 N.

4.7 **Standard ammonia solution –** Use stock ammonia solution and distilled water to prepare a calibration curve in a range appropriate for the concentrations of the samples.

5.0 PROCEDURE

To a 25 ml sample in a 50 ml Erlenmeyer flask, add, with thorough mixing after each addition, 1 ml phenol solution, 1 ml sodium nitroprusside solution, and 2.5 oxidizing solution. Cover samples with plastic wrap or paraffin wrapper film. Let colour develop at room temperature ($22^{o}C$ – $27^{o}C$) in subdued light for at least 1 hour. Colour is stable for 24 hours. Measure absorbance at 640 nm. Prepare a blank and at least two other standards by diluting stock ammonia solution into the samples concentration range. Treat standards the same as samples.

6.0 CALCULATION

Compare the samples absorbance with standard curve and note down the concentration.

B. AMMONIA BY DISTILLATION

The distillation and titration procedure is used especially for NH_3-N concentration > 5 mg/l. When sample contains high turbidity and organic nitrogenous matter, the following distillation method is used. This method should be used in industrial and highly polluted water.

Reagents :

Ammonia free distilled water: Use ammonia free distilled water for preparing all reagents and dilutions .

(i) **Borate Buffer Solution:** Dissolve 9.5 g sodium tetraborate $Na_2B_4O_7 10H_2O$ in approximately 500 ml distilled water. Add to this solution 88 ml 0.1 N NaOH and then dilute to 1 litre.

(ii) **Sodium Hydroxide (6 N):** Dissolve 240 g NaOH in 1 litre distilled water.

(iii) **Sodium Hydroxide (1 N):** Dissolve 4 g NaOH in 100 ml distilled water.

(iv) **Sulphuric Acid H_2SO_4 (1 N):** Dilute 28 ml of conc. H_2SO_4 to 1 litre with distilled.

(v) **Absorbing Solution (Plain Boric Acid):** Dissolve 20 g H_3BO_3 in distilled water & dilute to 1 litre.

(vi) **Mixed Indicator:** Dissolve 0.2 g methyl red in 100 ml 95% ethanol; and Dissolve 0.1 g methylene blue in 50 ml 95% ethanol. Mix both the solutions. This solution is stable for one month.

(vii) **Absorbing Solution Indicating Boric Acid:** Prepare by adding 10 ml mixed indicator & 20 g H_3BO_3 in 1 litre distilled water.

(viii) **Sodium Carbonate 0.05 N:** As alkalinity measurement.

7.0 PROCEDURE

(i) Dechlorinate the sample if residual chlorine is present, by adding 1 ml/mg of solution of (a) sodium thiosulphate (3.5 g dissolved in 1 litre) or (b) solution of sodium sulphite (0.9 g dissolved in 1 litre).

(ii) Arrange distillation apparatus of 500 ml capacity in such a manner so that outlet tip is submerged below the surface of the receiving boric acid. Use plain boric acid for nesslerization method or use indicating boric acid for titrimetric method.

(iii) Add 500 ml distilled water & 20 ml borate buffer to distillation flask and adjust pH to 9.5 with 6 (N) NaOH. Add few glass beads to the flask and boil for steaming out to remove traces of ammonia, if present. Cool & discard the solution continue distillation.

(iv) After steaming out, take 30 ml of dechlorinated sample or a volume diluted to 300 ml and add 25 ml borate buffer solution and adjust to pH 9.5 with 6 N NaOH using pH meter.

(iv) Collect approximate 200 ml distillate in 500 ml indicating or plain boric acid (for nesslerarition use plain boric acid and indicating boric acid for titrimetric method).

(vi) Take out the receiving flask when the required volume of approx. 250 ml distillate is collected (do not put off the heaters before removing the receiving flask other-wise back suction may occur).

(vii) Measure the exact volume of distillate and take a suitable portion for direct nesslerization or for titration with standard 0.02 N H_2SO_4 titrant until colour turns to pale lavender.

(ix) Carry out a blank through all steps for applying correction.

8.0 CALCULATION

$$NH_3\text{-N mg/l} = \frac{(A-B) \times 280}{\text{ml sample}}$$

A = Volume of H_2SO_4 (0.02 N) for sample titration
B = Volume of H_2SO_4 (0.02 N) for blank titration

9.0 REFERENCE

APHA (American Public Health Association), (1998), 20th Edition : Standard method for the examination of water and wastewater, 20th Edition, Washington D.C. USA. p. 4-103 – 4.109

14. PHOSPHATE

1.0 GENERAL

Phosphate may occur in surface or ground waters as a result of leaching form minerals or ores, from agricultural run off, industrial waste discharge and municipal sewage due to the utilization of synthetic detergents. Phosphorus occurs in natural waters and waste waters in the form of various phosphates. They are commonly classified as orthophosphate, condensed phosphates (meta---, pyro--, and poly phosphates) and organically bound phosphates. These various forms of phosphates may occur in soluble form or in particulate form.

2.0 PRINCIPLE

Molybdophosphoric acid is formed and reduced by stannous chloride to intensely coloured molybdenum blue. The method is applicable for lower level upto 7 µg P/L by use of increased light path length. Below 100 µg P/L an extraction step may increases the reliability and lessens interference. The minimum detectable concentration is about 3 µg P/L. This method is applicable for determination of phosphate in water and wastewater samples.

3.0 INTERFERENCES

Positive interference is caused by silica and arsenate only if the sample is heated. Negative interferences are caused by arsenate, fluoride, thorium, bismuth, sulphide, thiosulphate, thiocyanate or excess molybdate. Blue colour is caused by ferrous iron, but this does not affect results if ferrous iron concentration is less than 100 mg/L. Sulphide interference may be removed by oxidation with bromine water.

4.0 SAMPLE PRESERVATION

If dissolved phosphorous forms are to be differentiated, filter sample immediately after collection. Preserve by freezing at or below -10°C. Add 40 mg $HgCl_2$/L to the samples, especially when they are to be stored for long periods. (Caution: $HgCl_2$ is a hazardous - substance; take appropriate precautions in disposal; use of $HgCl_2$ is not encouraged).

5.0 APPARATUS

Spectrophotometer for use at 690 nm

Acid washed glassware : Clean all glassware with hot dilute. HCl and rinse well with distilled water. Preferably reserve the glassware only for phosphate determination. Avoid use of phosphate containing detergents for cleaning of glassware.

6.0 REAGENTS

Phenolphthalein indicator aqueous solution

Strong acid solution: Slowly add 300 ml concentrated H_2SO_4 to about 600 ml distilled water. When cool, add 4.0 ml concentrated HNO_3 and dilute to 1 L.

Ammonium molybdate reagent: Dissolve 25g $(NH_4)_6$ MO_7 $O_{24.}$ $4H_2O$ in 175 ml distilled water. Cautiously add 280 ml concentrated H_2SO_4 to 400 ml distilled water, cool, add molybdate solution and dilute to 1 L.

Stannous chloride reagent: Dissolve 2.5g fresh $SnCl_22H_2O$ in 100 ml glycerol. Heat in a water bath and stir with a glass rod to hasten dissolution.

Standard phosphate solution: Dissolve 219.5 mg anhydrous KH_2PO_4 in distilled water an dilute to 1000 ml; 1.0 ml = 50.0 µg PO_4^{3-}-P.

Working phosphate solution: Take 10 ml of standard phosphate solution into 100 ml volumetric flask and make upto 100 ml . It will be the 5 ppm PO_4-P.

Note: *All reagents should be prepared by phosphate free distilled water*

7.0 PROCEDURE

7.1 Preliminary Sample treatment: To 100 ml sample containing not more than 200 µg P and free from colour and turbidity, add 0.05 ml (1 drop) phenolphthalein indicator. If sample turns pink, add strong acid solution drop wise to discharge the colour. If more than 0.25 ml (5 drops) is required, take a smaller sample and dilute to 100 ml with distilled water after first discharging the pink colour with acid.

7.2 Preparation of calibration curve: Prepare calibration curve in the range of 0 – 0.6 mg/l PO_4 P by diluting 2, 4, 6, 8, 10 and 12 ml of working standard solution to 100 ml. This will be equal to the concentration of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mg/l PO_4-P.

7.3 Colour development: Add with thorough mixing after each addition, 4.0 ml molybdate reagent and 0.5 ml (10 drops) Stannous Chloride reagent. Rate of colour development and intensity of colour depend on the temperature of the final solution, each 1°C increase producing about 1 % increase in colour. Hence, hold samples, standards and reagents within 2°C of one another and the temperature range between 20 and 30°C.

7.4 Colour measurement: After 10 min. but before 12 minutes, using the same specific interval for all determinations, measure colour photometrically at 690 nm and compare with a calibration curve using a distilled water blank. Light path length may be increased for lower concentrations.

Always run a blank of reagents and distilled water because the colour at first develops progressively and later fades, maintain equal timing conditions for sample and standards. Prepare at least one standard with each set of samples or once each day that tests are made. The calibration curve may deviate from a straight line at the upper concentrations of the 0.3 to 2.0 mg/L range.

8.0 CALCULATION

Compare the reading of absorbance of samples with calibration curve and note down the concentration as mg/L PO_4-P, if any dilution is there, multiply it with the observed concentration and note down the final concentration as PO_4-P mg/L.

9.0 REFERENCE

APHA (American Public Health Association), (1998) : Standard method for examination of water and wastewater, 20th edition, Washington, DC, USA, P. 4.139 - 4.146.

Spectrophotometric determination of sulphate in rain water (Thorin method)

Applications

The method can be used to analyse SO_2 sampled in gas wash bottles containing dilute hydrogen peroxide, SO_2 sampled with impregnated filter (low detection limit), rain water or particulate matter. The measuring range is about 0.2 - 8 mg SO_4^{2-}/l.

Principle

A known amount of barium (Ba^{2+}) is added to the sample. Ba^{2+} reacts with sulphate (SO_4^{2-}) forming a solid precipitation according to: $Ba^{2+} + SO_4^{2-}$? $BaSO_4$. The excess Ba^{2+} concentration is measured with a metal ion indicator called Thorin. Thorin forms with Ba^{2+} a product with a red colour, which is measured spectrophotometrically. Unfortunately Thorin also reacts with other metal ions. They therefore have to be replaced by hydrogen ions prior to the determination. This is done by cationexchanging an aliquot of the rain sample. $BaSO_4$ is not insoluble in water, some SO_4^{2-} ions will remain after the Ba^{2+} addition. The solubility of $BaSO_4$ will therefore determine the lower detection limit for the method. The solubility of $BaSO_4$ is, however, much lower in organic solvents. Acetone or preferable dioxan is therefore added to the ionexchanged rainwater. Despite the dilution of the sample, the addition of an organic solvent will improve the lower detection limit. The linearity of the absorbance curve and thereby the detection limit is further improved by adding some SO_4^{2-} to the sample before the colour is measured. This is done by adding SO_4^{2-} to the Thorin solution.

Materials:
Spectrophotometer (520 nm),
pipettes,
volumetric flasks,
beaker,
ion exchange tube with a stopcock.

Chemicals:

Thorin: 2-(3,6-Disulfo-2-hydroxy-1-naphthylazo) benzenearsonic acid disodium salt ($C_{16}H_{11}AsN_2Na_2O_{10}S_2$).

0.005M sulphuric acid (from an ampoule)

$Ba(ClO_4)_2$ (p.a.)

$HClO_4$.

Adipic acid, $HOOC(CH_2)_4COOH$

1,4-Dioxane (purum, stabilised)

A strong cation exchange resin in H^+ form e.g. Dowex 50WX8 50-100 mesh

Solutions

Thorin solution
Dissolve 250 mg Thorin in 10 ml 0.01 N (0.005M) sulphuric acid and some distilled (de-ionised) water. Dilute with distilled water to 100 ml. This solution is stable for two days.

Barium stock solution
Dissolve 525 mg dehydrated $Ba(ClO_4)_2$ (p.a.) in 250 ml 0.1 M $HClO_4$ (add 3.6 g or 2.2 ml 70% $HClO_4$ to 250 ml)

Barium solution

Dissolve 10 g adipic acid, $HOOC(CH_2)_4COOH$, in about 0.5 litre dioxane. Add 10 ml of the barium stock solution. Dilute to 1 litre with dioxane.

Standard solutions

100 mg SO_4^{2-}/l: Dilute 20.8 g or 20.8 ml 0.01 N (0.005M) sulphuric acid to 100 ml.
Make 6 standards (0.5, 1, 2, 4 and 8 mg SO_4^{2-}/l) by diluting 0.5, 1, 2, 4, 6 and 8 ml of the stock solution to 100 ml with water respectively.

Ion exchange

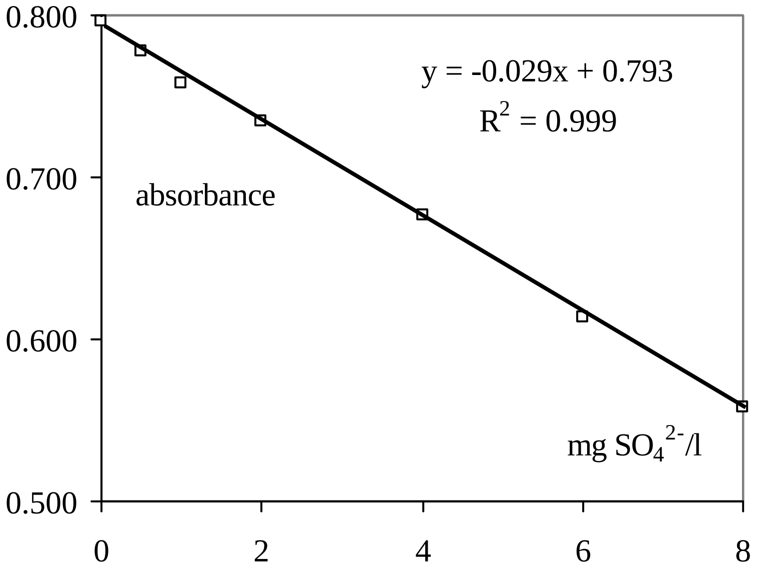
Samples containing other cations than H^+ has to be cat ion exchanged prior the spectrophotometric detection (e.g. rain water and leached PM_{10} filters). Use an ion exchange tube with a stopcock. Fill the column with water and add the resin (strong cation exchange resin in H^+ form e.g. Dowex 50WX8 50-100 mesh). The water level should always be above the resin. Fill the exchange tube with water and empty it a couple of times to rinse the resin. When a sample is added it is important to discard the first eluate (a volume larger than the resin volume). Fill the exchange tube with sample again and analyse the sample according to the description below.

Analysis

Set the wavelength to 520 nm and let the spectrophotometer run for half an hour before analysis. Make a standard curve by mixing 2 ml standard solution with 5 ml barium solution and 0.125 ml Thorin solution in a large (about 50 ml) beaker. Pour the solution into the measuring cell and read the absorbance. The absorbance is usually not so stable, but decreases with time. Wait some seconds until it is almost stable. Repeat this at least twice (or until a constant absorbance is obtained). You can use the same beaker all the time if you empty it between each addition. Use de-ionised water as zero concentration. A typical standard curve can look as below:

mg/l	absorbance
0	0.796
0.5	0.778
1	0.758
2	0.734
4	0.677
6	0.613
8	0.558

Plot the XY curve (scatter plot):



You can calculate the concentrations using the linear regression equation. If the calculated concentrations deviate less than 0.2 mg/l from the expected, the standard curve is OK A single standard can be excluded from the calculations if it deviates too much and the rest of the standards are good. This can be done automatically in Excel:

mg/l	absorbance	calculated
0	0.796	-0.12
0.5	0.778	0.49
1	0.758	1.17
2	0.734	1.99
4	0.677	3.92
6	0.613	6.09
8	0.558	7.96
slope	-0.029	
intercept	0.793	
r^2	0.999	
S.D.	0.003	

Continue with your samples. Mix the solutions twice and use the second reading. Let Excel calculate the concentrations. Every now and then you have to check the absorbance with a sulphate standard. If the concentration of the sample exceeds that of the standard with highest concentration (8 mg SO_4^{2-}/l), the sample has to be diluted and analysed again.

CENTRAL POLLUTION BOARD- DELHI
LABORATORY DIVISION

GLOSSARY OF TERMS ON

LABORATORY QUALITY ASSURANCE (QA) AND QUALITY CONTROL (QC) SYSTEM

1.	Accreditation	Formal recognition of the competence of a body or an organization for a well-defined purpose. It is the procedure by which a laboratory is assessed to perform a specific range of test or measurements
2.	Accuracy	The closeness of agreement between the "true" value and the measured value. The smaller the systematic error of the analysis is, the more accurate is the analytical procedure. It is assessed by means of reference samples and percent reconveries.
3.	Audit Sample	Prepared reference sample inserted into the sample processing procedure as close to the beginning as possible.
4.	Background Sample	A sample taken from a location on or proximate to the site of interest and used to document baseline or historical information
5.	Bias	Systematic error, consistent deviation of measured values from the true value.
6.	Calibration	In chemical measurement, Calibration refers to the process by which the response of a measurement system is related to the concentration or the amount analyze of interest
7.	Calibration Laboratory	Laboratory that performs calibration.
8.	Calibration Method	Defined technical procedure for performing a calibration.
9.	Calibration Standards	A series of known standard solutions used by the analyst for calibration of instrument (i.e. preparation of the analytical curve).
10.	Certified Reference Material (CRM)	A certified reference material or substance whose property or properties can be defined so exactly that it may be used for the calibration of measuring instruments, the check of results obtained form measuring testing and analytical processes, and for the characterization of substance properties.
11.	Chain of Custody (COC)	Documentation of the history of the sample. The components of chain of custody are sample seals, log book, record and sample analysis request sheet and the procedures used for estimation.
12.	Confidence Interval	Set of possible values within which the true value will lie with a specified level of probability.
13.	Confidence Limit	One of the boundary values defining the confidence interval
14.	Contamination	Something inadvertently added to the sample during the sampling or analytical process.
15.	Control	Type of sample against which the results of a procedure are judged.
16.	Conventional true value	Value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose
17.	Data Quality Objectives (DQOs)	Statements on the level of uncertainty that a decision-maker is willing to accept in the results derived from environmental data.
18	Environmental sample	An environmental sample or field sample is a representative sample of any material (aqueous, nonaqueous or multimedia) collected from any source for which determination of composition of contamination is requested or required.
19.	Error	Difference between a measured value and the true value.
20.	Good Laboratory Practice (GLP)	Good laboratory Practice (GLP) is concerned with the organizational process and the conditions under which laboratory studies are planned, monitored, recorded and reported
21.	Gross error	Which makes it necessary to begin a new analysis (Ex. Using a wrong reagent, taking a wrong pipette, measuring at a wrong wavelength, instrument breakdown, heavily contaminated glassware

		etc.). These errors should easily be recognized.
22.	Instrumentation Detection Limit	The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wave length
23.	Inter Laboratory Precision	(Reproducibility) Variation associated with two or more laboratories or organizations using the same measurement method.
24.	Inter Laboratory Test	A series of measurements of one or more quantities performed independently by a number of laboratories on samples of a given material (other terms: Round robin test, Collaborative trial, Collaborative reference program, Collaborative analytical study, ring test).
25.	Interferences	Compounds whose presence obscures the measurement of the analyte of interest by the introduction of an unrelated analytical signal where the analyte is measured.
26.	Internal Quality Control	Internal quality control encompasses all measures, which are planned, ordered and executed by a laboratory itself.
27.	Intra-laboratory Precision	(Repeatability) Variation associated with a single laboratory or organization
28.	Limit of detection (LOD)	The LOD of an individual analytical procedure is the lowest analytical amount of an analyte in a sample, which can be detected but not necessarily quantified as an exact value. For many purposes, the LOD is arbitrarily taken to be $3s_b$ or 3 x the standard deviation of the blank value or of background
29.	Limit of determination	The lower level where measurements become arbitrarily meaningful and is defined arbitrarily as LOQ-$10s_b$ (10 x the standard deviation of the blank value or of background) At this concentration, the relative confidence in the measured value is ± 30% at the 95% confidence level.
30.	Limit of Quantitation (LOQ)	The constituent concentration that produces a signal sufficiently greater than it can be detected within specified limits by good laboratories during routine operating conditions. Typically it is the concentration that produces a signal time 10s above the reagent water blank signal.
31.	Matrix	The matrix of a material is the totality of all parts of a material and their chemical and physical properties including mutual influences.
32.	Matrix/ Spike Duplicate Analysis	In matrix/spike duplicate analysis, predetermined quantities of shock solutions of certain analytes are added to a sample matrix prior to sample extraction/digestion and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision. The concentration of the spike should be at the regulatory standard level or the estimated or actual method quantification limit. When the concentration of the analyte in the sample is greater than 0.1% no spike of the analyte is necessary.
33.	Method Detection Limit (MDL)	The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in given matrix containing analyte which has processed through the pre-operative procedure
34.	Method Quantification Limit (MQL)	The Method Quantification Limit is the minimum concentration of a substance that can be measured and reported.
35.	Optimum Concentration Range	A range defined by limits expressed in concentration, below which scale must be used and above which curve correction should be considered. This range varies with the sensitivity of the instrument and the operating conditions employed.
36.	Outlier data	The data which are suspected to be extremely low or high from the expected value or mean.
37.	Precision	The closeness of agreement between the results obtained by applying the experimental procedure several times under prescribed

		conditions. (The smaller the random part of the experimental errors which affect the results, the more precise is the procedure). Within run and between day precision have to be considered. (see repeatability and reproducibility)
38.	Proficiency Testing	Determination of the laboratory calibration or testing performance by means of inter-laboratory comparisons.
39.	Protocol	Thorough written description of the detailed steps and procedures involved in the collection of samples.
40.	Quality Assessment	Procedure for determining the quality of laboratory measurements by use of data from internal and external quality control measures.
41.	Quality assurance	All those planned and systematic actions necessary to provide adequate confidence that a product or a service will satisfy given requirements for quality.
42.	Quality Assurance Programme Plan (QAPP)	An orderly assemblage of management policies, objectives, principles and general procedures by which an organization involved in environmental data generation activities outlines how to produce data of known quality.
43.	Quality Assurance Project Plan (QAPjP)	An orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the DQOs for a specific data collection activity.
44.	Quality Characteristic	The characteristics and characteristic values (or expressions) of something (e.g. a method, a piece of equipment, a measurement result etc.) in relation to their suitability to fulfill set requirements.
45.	Quality Control	Set of measures within a sample analysis methodology to assure that the process is in control.
46.	Quality Control Charts	A Quality control chart is a sequential plot of some quality characteristic. It may be a day by day measurement of any interest of analyte (e.g. COD or BOD or Nitrate). The Chart consists of central line and two pairs of limit lines, the Upper and Lower Control Limits (UCL., LCL) Example : Shewart's Quality Control Chart
47.	Quality Manual	A document stating the quality policy, quality system and quality practices of an organization.
48.	Quality System	The organizational structure, responsibilities, procedures, processes and resources for implementing quality management.
49.	Random Errors	Random errors are indicated by the scatter of the results of repeated measurements on the aliquot of same sample about the mean value. The sign and magnitude of the error of any particular result varies at random and cannot be known exactly. Random errors arise from uncontrolled variations in the conditions of the analytical system (factors like analyst, equipment, instrument, method, quality of glassware and chemicals, reagents etc.,) during different analysis.
50.	Range	Spread of values calculated by subtracting the lowest value from the highest value
51.	Reagent Blank	A reagent blank is an aliquot of analyte – free water or solvent analysed with the analytical batch.
52.	Reference material	A material or substance one or mare of whose property value are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning value to materials
53.	Reference Standard	A standard, generally of the highest meteorological quality available at a given location, from which measurements made at that location, is derived.
54.	Relative Standard Deviation (RSD)	Estimate of the average error in the measurement due to unassignable causes and usually expressed as a percentage of the average sample concentration.
55.	Repeatability	The closeness of agreement between successive results obtained with the same method on identical test material under the same condition. (Same operator, same apparatus, same laboratory and short intervals of time) can also be interpretable as within – run precision.
56.	Replicate Sample	A replicate sample is a sample prepared by dividing a sample into

		two or more separate aliquots. Duplicate sample is considered to be two replicates.
57.	Reproducibility	The closeness of agreement between individual results obtained with the same method and on identical material but under different test conditions (different operator, different time's etc.) Can also be interpreted as "Between-run precision".
58.	Sample Holding Time	The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.
59.	Sampling	Attempt to choose and extract a representative portion of a physical system from it's surroundings.
60.	Sensitivity	Sensitivity describes the ability of an experimental method to differentiate between related values (e.g. concentrations). It indicates to which degree value changes depending upon the signal of the measuring system and can be quantified using the slope of the calibration curve.
61.	Standard Curve	A standard curve is a curve, which plots concentrations of known analyte standard versus the instrument response to the analyte.
62.	Standard Deviation	Square root of the variance (statistical analysis).
63.	Standard Methods	A standard method is an acknowledged analytical method according to an international or national standard or guidelines or to a given legal statue.
64.	Standard Operating Procedure (SOP)	Standard Operating procedure (SOP) means written procedure which describes how those routine laboratory operations are to be performed.
65.	Stratified Random	Sampling technique in which estimates of strata means are combined to yield estimates of the population mean.
66.	System Blank	(Instrument Blank): Measure of the instrument background or baseline response in the absence of a sample.
67.	Systematic Error	Systematic errors are indicated by a unidirectional tendency of results, which could be greater or smaller than the true value. When systematic error is present, the result are said to be biased (bias = systematic error) Systematic error in analytical results may occur when: method used is not specific for the analyte; due to presence of some interfering substances; improper performing of the analysis, instability of samples between sample collection and analysis.
68.	Test	A technical operation that consists of the determination of one or more characteristics or performance of a given product, material equipment organism, physical phenomenon, process or service according to a specified procedure.
69.	Test Method	Defined technical procedure for performing a test
70.	Traceability	The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons.
71.	True value	Real amount or concentration of an analyte in a certain sample. It is an ideal value, which could be arrived at only if all causes of measurement error were eliminated. The amount or concentration given for an analyte in a certified reference material is a good substitute for the true value.
72.	Trueness	The closeness of agreement between the average value obtained from a large series of test results and an accepted reference value
73.	Uncertainty of measurement	Parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand
74.	Validation	Validation is the total testing procedure if an analyzing real samples.
75.	Variance	Measure of the variability in a population / set of analytical data. It is the square root of the standard deviation