Technical Assistance
HYDROLOGY PROJECT

World Bank & Government of The Netherlands funded

Training module # WQ - 33

Use of Ion Selective Probes

New Delhi, February 2000

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DHV Consultants BV & DELFT HYDRAULICS

with
HALCROW, TAHAL, CES, ORG & JPS

Table of contents

1. Module context

This module discusses the use of ion selective electrodes recommended for water quality analysis under the Hydrology Project. Modules in which prior training is required and other related modules are listed below.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

No.	Module title	Code	Objectives
1.	Basic chemistry concepts	**WQ - 02**	• Convert units from one to another • Discuss the basic concepts of quantitative chemistry • Report analytical results with the correct number of significant digits.
2.	Understanding the hydrogen ion concentration (pH)	**WQ - 06**	• Discuss about the concept of pH • Calculate pH
3.	Understanding chemical oxygen demand test	**WQ - 18**	• Appreciate significance of COD measurement • Understand the chemistry of COD measurement
4.	Basic aquatic chemistry concepts	**WQ - 24**	• Understand equilibrium chemistry and ionisation constants. • Understand basis of pH and buffers • Calculate different types of alkalinity.
5.	Advanced aquatic chemistry: solubility equilibria	**WQ - 29**	• Explain the principles of chemical equilibrium • Define solubility product and explain how this relates to water quality assessment • Define the octanol-water partition coefficient and explain how this relates to water quality assessment.
6.	Advanced aquatic chemistry: redox equilibria	**WQ - 30**	• Understand the principles of redox reactions • Understand the significance of redox potential measurement
7.	Potentiometric Analysis	**WQ - 32**	• Understand the principles of potentiometric analysis • Understand construction of reference and indicating electrodes

2. Module profile

Title : Use of Ion Selective Probes

Target group : HIS function(s): Q2, Q3, Q5, Q6

Duration : One session of 45 min

Objectives : After the training the participants will:
- understand precautions required in use of ion selective electrodes

Key concepts :
- ion selective electrodes recommended under HP
- calibration
- precaution

Training methods : Lecture, exercises

Training tools required : Board, flipchart

Handouts : As provided in this module

Further reading and references :
- Chemistry for environmental engineers - C. N. Sawyer, P. L. McCarty & G. F. Parkin, McGraw - Hill, Inc., 1994
- Standard methods for the examination of water and wastewaters, AWWA, 19th edition, 1995

3. Session plan

No	Activities	Time	Tools
1	***Preparations***		
2	***Introduction***: • Discuss various types of indicating electrodes and probes	5 min	OHS
3	***Performance characteristics*** • Describe precautions, limitations and advantanges of potentiometric measurements using indicating electrodes and probes • Discuss calibration requirements and methods	15 min	OHS
4	***Electrodes and probes recommended under HP*** • Discuss applications of the recommended probes and procedures for their use.	15 min	OHS
5	***Wrap up*** • Discuss experience of participants, if any • Review precautions and limitations	10 min	

4. Overhead/flipchart master

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 24-26, maximum two levels
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/Equations	OHS-Equation	Use of a table will ease horizontal alignment over more lines (columns) Use equation editor for advanced formatting only

Ion selective probes (1)

- Electrode potential is linearly related to log of activity of ion
- Glass electrode for H^+ measurement is most commonly used.
- Probes for DO, F^-, NH_3 and CN^- recommended under HP

Types and examples

• Glass membrane	Na^+, K^+, H^+, NH_4^+
• Liquid membrane	NO_3^-, Ca^{2+}, Mg^{2+}
• Solid membrane	S^{2-}, F^-, CN^-, Pb^{2+}
• Diaphragm	NH_3, O_2, HCN
• Metal	Ag^+, Cu^{2+}, Cd^{2+}, I^-

Performance characteristics (1)

- Temperature effect
  - *calibration standard and sample at same temperature*
  - *meter in-built correction*
- Response time
  - *steady value, few seconds to minutes*
- Potential drift
  - *recalibrate frequently*

Performance characteristics (2)

- Sensitivity
  - *working range, depends on properties of membrance*
  - *response 59.15 mV per ten fold conc. change for one electron.*
- Selectivity and interference
  - *other ions may effect reading*
  - *remove interfering ion*
  - *calibrate in presence of the ion.*

Performance characteristics (3)

- Activity vs. concentration
  - *measures activity*
  - *calibration standard of similar ionic strength.*
- pH
  - *may affect ionisation*
  - *formation of complexes*

Performance characteristics (4)

- Presence of complexing agent
  - *electrodes measure free ions*
  - *remove complexing agents*
- Life time
  - *rate of leaking of liquid ion exchanger*
  - *chemical fouling of solid membranes*

Advantages

- turbid samples
- small volume, sample not destroyed
- do not change existing equilibria
- direct reading of conc. over wide range
- sample does not require pretreatment
- rapid response
- ideal for on-line measurement

Electrode calibration

- Calibration curve
  - *treatment of sample and standard for adjustment of pH and ionic strength*
- Standard addition
  - *when effect of ions in sample matrix can not be duplicated in standard*
  - *significant liquid junction potential*

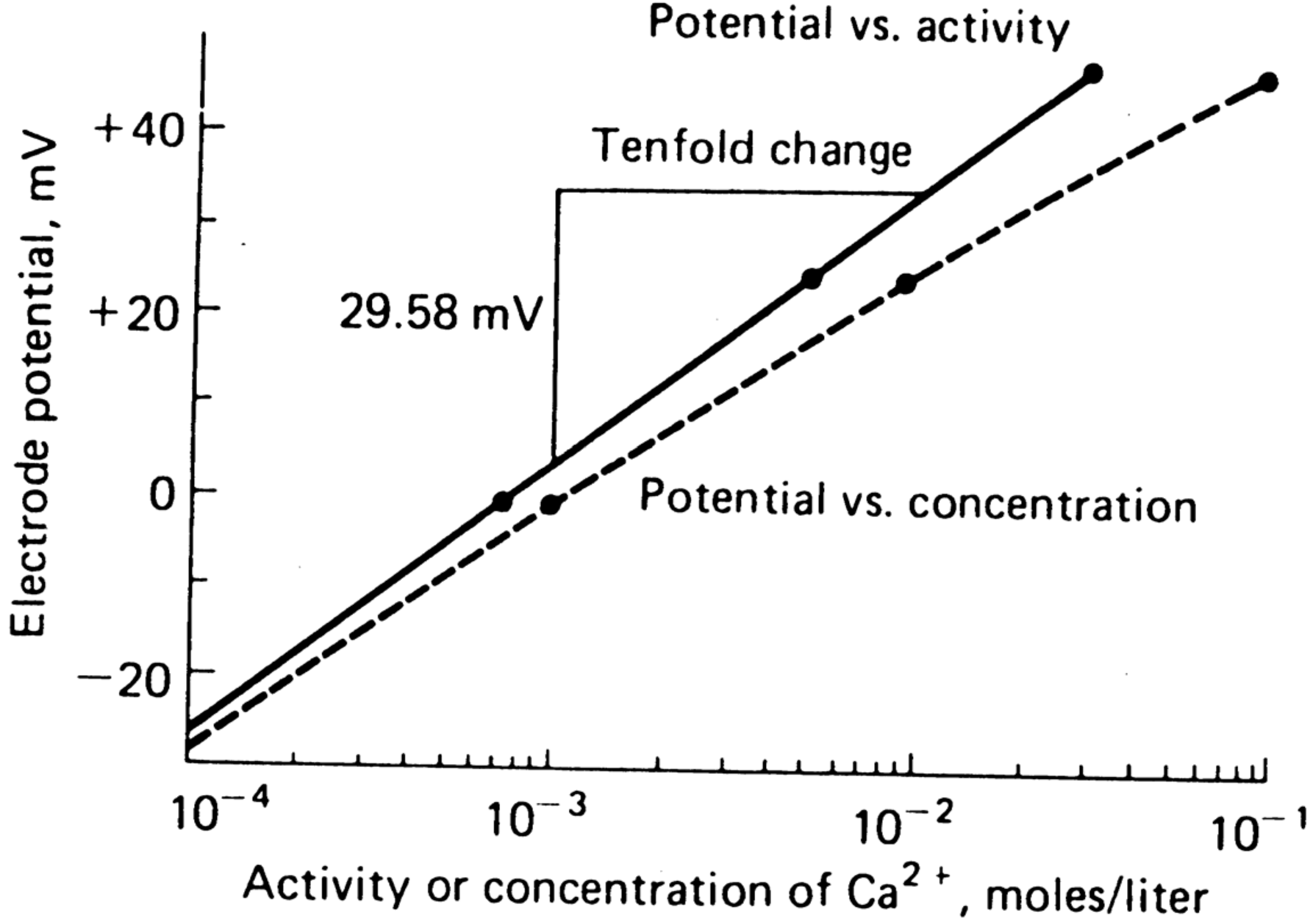

Figure 1 Response of Ca electrode as functions of Ca^{++} ion concentration and activity

Standard addition

- $E_{obs} = E_{ref} + E_j - E_{ind}$

  which can be written as:

$$-\log a = \frac{E_{obs} - K}{0.0591 / n}$$

- K is the unknown change in potential
- Observe potential before and after adding known standard to sample and solve for 'a', the analyte concentration

Dissolved oxygen probe

- Site and on-line measurements
- Frequent calibration
  - *air*
  - *water of known DO*
- Fouling of membrane
  - *change when response is sluggish*
  - *do not trap air bubble*
- Sample flow across membrane while measuring

Fluoride electrode

- Evaluate suitability critically
- Al^{3+} and Fe^{2+} cause interference
- At pH < 5, HF.HF is formed
- Add complexing agent and pH buffer

Ammonia probe

- Wide range, 0.03 - 1400 mg/L
- Interference due to amines, Hg & Ag
- Increase pH to convert NH_4^+ to NH_3
- Stir sample slowly.

Nitrate electrode

- Alternative to UV method and convenient compared to Cd reduction method
- Adjust pH to 3 eliminate HCO_3^-
- Requires complexing agents for other interfering ions
- Check calibration frequently

Cyanide electrode

- Distillation of sample is required
- Range 0.025 - 10 mg CN^-/L
- Response time at least 5 min, mix well
- Do not work with acidified sample in open, HCN is extemely toxic gas

5. Evaluation sheets

6. Handout

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Add copy of Main text in chapter 8, for all participants.

7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

8. Main text

Contents

Use of Ion Selective Probes

1. Introduction

Ion-selective electrodes belong to a class of electro-chemical sensors which respond to only the ion of interest. Their use involves a special case of direct potentiometry. When these electrodes are placed in a conducting solution, they generate a millivolt potential related to the concentration of the ion. The potential is linearly related to log of concentration of the ion. To be more accurate, the term ion 'activity' should be used instead of concentration. For simplicity, this text will use the term concentration, which in most cases is a close approximation of activity.

Historically, the oldest and the best known and most widely used ion-selective electrode is the glass electrode, which responds to hydrogen ion activity. It remained the only sensing electrode until mid 1960's. But the renewed interest in potentiometry has now led to the commercial availability of a range of ion-selective electrodes.

Basic principles of redox reactions and construction of various types of indicating electrodes and probes are discussed in module # 30, 'Advanced Aquatic Chemistry Concepts: Redox Equilibria, and module # 32, 'Potentiometric analysis'. This module describes general aspects of ion selective probes and use of DO, F^-, NH_3^- and CN^- probes which are recommended under Hydrology Project.

Table 1 gives an overview of indicator electrodes commonly available

Table 1: Types and examples of ion electrodes

Types of electrode	Description	Examples of chemical specie measured
Glass membrane electrode	Electrode having glass sensing membrane	Na^+, K^+, H^+, NH_4^+
Liquid membrane electrode	Electrode having sensing membrane comprising an ion exchange liquid held in a rigid porous membrane	NO_3^-, Ca^{2+}, Mg^{+2}, NH_4^+
Solid membrane electrode	Selective electrode having sensing membrane made of poorly soluble metal salt monocrystal or metal salt powder	S^{2-}, F^-, CN^-, Pb^{2+}, Ag^+
Diaphragm electrode:	Electrodes combining gas transmitting membrane and pH electrode or ion electrode	NH_3, HCN, O_2
Metal electrode	Electrode comprising the metal or the metal and a poorly soluble salt.	Ag^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, I^-

2. Performance characteristics of electrodes

Temperature effect:
It is necessary to correct for the temperature of the samples because the electrode potential is temperature dependent. The sample temperature should be measured independently and a temperature correction should be made with the in-built correction in the meter.

Response time:
The response time of ion-selective electrode is the speed at which it responds (electrode potential reaches a steady state value), and depends upon the type of electrode and concentration of ion under measurement. The response time of solid – state electrode is generally of the order of 5-10 seconds. The response time of some liquid ion-exchanger electrode is longer, usually many seconds or even few minutes at low concentrations. When making a reading, enough time must be given for the electrode to reach a stable reading.

Potential drifts:
The potential drifts of ion-selective electrodes is connected with changes in the surface structure of solid – membrane electrode due to contact with the electrolyte and due to dissolution of the ion exchanger of liquid-membrane electrodes. All electrodes show drifts with time and therefore need re-calibration periodically with standardising solutions. This should be done every few hours if making many analyses.

Sensitivity:
The useful working range of the ion-selective electrodes is knows as sensitivity which is effectively governed by the properties of the membrane. The working range of electrode is determined from the concentration (mg/l) to which an electrode responds in a theoretical fashion (59.15 mV/ten fold change in concentration when one electron is involved in the reaction).

Selectivity & Interferences:
Although intended to be specific to a single ionic species, most electrodes respond in varying degrees to the presence of other ions. Where severe interferences are likely to be encountered, there are two practical courses of action. Either the electrode must be calibrated in the presence of interfering ion or the interference must be eliminated by some other means such as buffering, precipitation or by adding a complexing agent.

Activities vs. Concentration:
Electrodes measure activities and not concentrations. The activity varies with ionic strength. Thus, to use an electrode for concentration measurements, the electrode must be calibrated in a standard solution of similar ionic strength (see section 3. Electrode calibration).

Effect of pH:
The pH of the sample solution changes the chemistry of the analyte ion. For instance, at low pH values F^- ions are present as HF, which are not sensed by the fluoride electrode. Thus in such cases an appropriate pH adjuster should be added to samples to set up a reliable ion-selective electrode analysis.

Presence of complexing agent:
A number of ions in water samples can be present in more than one form, such as complexes with other ions or molecules. Electrodes measure only the free ion in solution, and cannot sense bound or complexed ions.

Life - time:
The life-time of an electrode is determined by the rate at which the liquid ion exchanger leaks through the membrane in liquid membrane electrodes, or the time required for crystal surface or the pressed pellet to become chemically fouled in solid membrane electrodes. Life-time markedly depends upon conditions of use. With good care, electrodes should provide many months or years of service. If electrode response drops off, rejuvenation of electrodes is possible by refilling the liquid internals, replacing sensing membrane of liquid membrane type electrode or mechanical polishing of solid – state membrane tip.

The use of ion-selective electrodes as an analytical techniques in water analysis is increasing. This is because of the significant advantages such as:

- They are not bothered by turbidity or colour of the sample
- Small volumes of samples can be analysed without loss of sample
- Measure species without upsetting chemical equilibrium
- Measurements are independent of volume of sample
- Concentrations can be read directly on specific ion meter
- Calibration curves can cover even six decades of concentration
- Electrodes are sensitive up to parts per billion

Further application of these electrodes especially for on-line analysis are very much in use because:

- They do not usually require extensive pre-treatment of the sample
- They have a relatively rapid response-time
- They provide an electrical analogue signal which does not need sophisticated signal conditioning circuits before a result can be displayed to the instrument user
- Considerable previous experience of on-line instrumentation for pH measurement is available, which is relevant to other electrodes also.

3. Electrode calibration

Activity vs. concentration:
Electrode response is related to analyte activity rather than to analyte concentration. More often than not, activity coefficients are not available. The difference between activity and concentration is illustrated by Figure 1 in which the response of a calcium electrode is plotted against logarithmic functions of the calcium concentration and calcium activity. The electrode responds in an ideal fashion, i.e., constant slope, only when concentration values are changed to activity values.

An obvious way to convert potentiometric measurements from activity to concentration is to make use of an emperical calibration curve, such as the lower plot in Figure 1. For this approach to be successful, it is necessary to make the ionic composition of the standards essentially the same as that for the analyte solution. This is often done by swamping both sample and standards with a measured excess of an inert electrolyte, thus making the added effect of electrolyte from the sample matrix negligible.

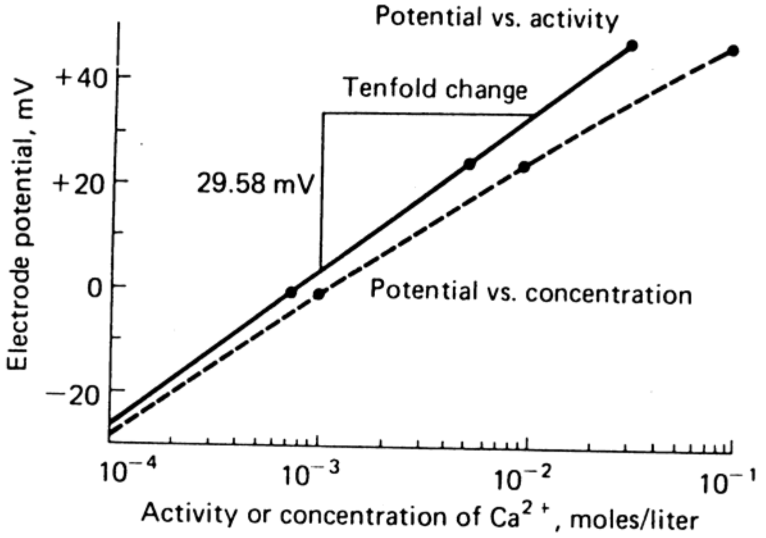

Figure 1 Response of Ca electrode as functions of Ca^{++} ion concentration and activity

Standard addition method:

Notwithstanding the advantages of direct potentiometric measurements, there are certain inherent limitations to the method. Principal among these is the existance of a 'liquid junction potential' that affects most potentiometric measurements. The junction potential, E_j, is created at the interface of the electrode and the analyte solution due to unequal mobility of various cations and anions, which modifies the observed potential, E_{obs}, according to the following expression

$$E_{obs} = \left(E_{ref} + E_j - E_{ind}\right) = E_{ref} + E_j - \left[E^0 - \frac{0.0591}{n}\log\frac{1}{a}\right] \qquad (1)$$

$$-\log a = \frac{E_{obs} - K}{0.0591/n}$$

where a is the analyte activity, E_{ind} is the actual indicator electrode potential and K is a constant.

In case the effect of liquid junction potential is to be eliminated and where the effect of the matrix of the sample cannot be swamped by addition of an inert electrolyte, standard addition method may be used. It involves determining the potential of the electrode system before and after a measured volume of a standard has been added to a known volume of the analyte solution. As in the other method, if required, an excess of an electrolyte is added to the analyte solution to prevent a major shift in the ionic strength due to addition of the standard. The following example explains the calculations involved in the method.

Example 1:

A lead ion electrode developed a potential of 0.4706 V (vs. Standard Calomel Electrode) when immersed in 50.00 mL of a sample. A 5.00 mL addition of standard 0.02000 M lead solution caused the potential to shift to 0.4490 V. Calculate the molar concentration of lead in the sample.

Applying Equation 1 and assuming that the activity of Pb^{2+} is approximately equal to its molar concentration C_x, we may write

$$-\log C_x = \frac{E_1 - K}{\frac{0.0591}{2}}$$

Where E_1 is the measured potential (0.4706 V).

After introduction of the standard addition, the potential is now E_2 (0.4490 V) and

$$-\log \frac{50.00 \text{ X } C_x + 5.00 \text{ X } 0.02000}{50.00 + 5.00} = \frac{E_2 - K}{\frac{0.0591}{2}}$$

which can be written as

$$-\log (0.9091\, C_x + 1.818 \text{ X } 10^{-3}) = \frac{E_2 - K}{\frac{0.0591}{2}}$$

Subtraction of this equation from the first gives

$$-\log \frac{C_x}{0.9091\, C_x + 1.818 \text{ X } 10^{-3}} = \frac{2(E_1 - E_2)}{0.0591}$$

$$= \frac{2(0.4706 - 0.4490)}{0.0591} = 0.7310$$

$$\frac{C_x}{0.9091\, C_x + 1.818 \text{ X } 10^{-3}} = 0.1858$$

$$C_x = 4.06 \text{ X } 10^{-4} \text{M}$$

4. Recommended probes under HP

This section describes the use of probes recommended under HP. As stated earlier, while the probes have their advantages, their limitations must also be kept in mind when used in different situations.

For each case the manufacturer's instructions for calibration and operation of the probe and the ion-meter should be followed.

4.1 Dissolved oxygen probe

Application:
DO probes are useful for on site measurements and when a large number of samples are to be analysed in the laboratory, for example, when determining BOD. For continuous DO measurement the potentiometric measurement is the only option.

Construction:
The probe consists of two solid metal electrodes in contact with a supporting electrolyte separated form the test solution by a selective membrane permeable to molecular oxygen.

Interference:
The probe exhibits a high temperature coefficient. The ion-meter may have in-built temperature correction or correction factor may be available from the manufacturer. Prolonged use of the probe in waters containing sulphides lowers the sensitivity of the probe.

Calibration:
The probe may be calibrated by reading against air, a sample containing known DO concentration (determined by iodometric titration) or a sample containing zero DO (by adding sulphite to the sample). Periodic cross-check of calibration by different methods is recommended. Preferably calibrate using the sample water. In case the sample water contains interfering substances, calibrate with a sample of clean water containing approximately the same salt content.

Precautions:
Change the probe membrane when the response becomes sluggish or erratic. Take care to avoid contamination of the sensing element and trapping of minute air bubbles while changing the membrane. Provide sufficient sample flow across the membrane surface while making measurements.

4.2 Fluoride electrode

Applications:
Fluoride electrode has been used for determination of fluoride in drinking water supplies. The analyst should be aware of its limitations as described in the section on interferance below. Its suitability should be evaluated since even small errors can be critical in terms of suitability of a water for drinking purpose.

Construction:
The key element in the fluoride electrode is the lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations, in the sample and the standard solution in the electrode. The electrode can be used with a standard calomel reference electrode.

Interference:
Fluoride forms complexes with several cations notably aluminium and iron. At pH values lower that 5 poorly ionisable HF.HF complex is formed. Cyclohexylene-diamine-tetra acetic acid and a buffer can be added to the sample to complex the interfering ions. The buffer maintains a pH of 5. This pH also reduces the effect of the interfering ions. Samples having TDS in excess of 10,000 mg/L should be distilled.

Calibration:
A calibration curve in the 0.2 to 2 mg/L F^- range may be prepared. The recommended complexing agent and buffer should be added to the sample as well as the standards. This would make the ionic strength of the sample similar to that of the standard.

Precautions:
Treat the sample and the standard as described above. Avoid stirring before immersing electrode so as not to entrap air bubbles. Let electrode remain in solution until the reading is constant. Recalibrate frequently against atleast one standard.

4.3 Ammonia probe

Applications:
The method can be used for a wide range of ammonia concentration from 0.03 to 1400 mg/L NH_3-N. It is suitable for coloured and turbid water samples.

Construction:
The probe consists of a pH electrode and a reference electrode. It is provided with a membrane which allows permeation of NH_3. The permeated gas reacts with an internal solution and changes its pH, which is sensed by the pH electrode.

Interference:
The probe has a high temperature coefficient. The temperature correction is generally available from the manufacturer. Amines cause a positive interference. Hg and Ag form complexes with ammonia. This can be overcome by adding NaOH/EDTA to the sample.

Calibaration:
Calibrate the instrument using a series of standards in the range of 0.1mg/L - 1000 mg/L NH_3-N prepared from NH_4Cl. Sufficient quantity of NaOH is added to convert NH_4^+ to NH_3. In case presence of Hg or Ag is suspected in the sample ass NaOH/EDTA solution to the standard also. Same volume of the reagent should be added to the standards as well as the sample. A 10 fold increase in NH_3 concentration the potential change should be about 59mV.

Precautions:
Calibration standards and samples should be at the same temperature. Do not add NaOH before immersing the probe to avoid loss of ammonia. Stir slowly and maintain the same speed while taking readings. For ammonia concentration below 1mg/L, 2 to 3 minutes may be required to obtain a stable response from the electrode.

4.4 Nitrate electrode

Applications:
Potentiometric analysis for nitrate is an alternative to UV absorption method where presence of organic matter in the sample interferes with the spectrophotometric method. It is also convenient and time saving when compared to cadmium reduction method. The use of the electrode may be limited in case of saline samples (see interferences below). The electrode responds to NO_3^--N concentration in 0.14-1400 mg/L range.

Construction:
The electrode has a sensitive liquid ion-exchange membrane held in an inert membrane. It develops a potentia across the membrane whose one face is kept in contact with the analyte in the sample and the other in contact with an inner standard solution.

Interferences:
Chloride and bicarbonate ions interfere when their weight raios to NO_3^--N are in excess of 10 and 5, respectively. Variation in pH gives erratic response. Other ions which may interfere are NO_2^-, CN^-, S^{2-}, Br^-, I^- and NO_2^-.

Calibration:
A buffer is added to the standards and the sample to adjust the solutions to similar ionic strength. The buffer maintains a pH of 3, which eleminates HCO_3^-. The buffer also contains $Ag_2(SO_4)$ to remove interference from Cl^-, Br^-, S^{2-}, and CN^-, and sulfamic acid to remove NO_2^-.

Precautions:
The standards and the samples should be at same temperature preferably 25^0C. The calibration curve, when mV potential reading is plotted as ordinate versus log NO_3^--N concentration as abscissa, should result in a straight line with a slope of +57±3mV/decade. Check the electrode calibration several times a day using at least one standard.

4.5 Cyanide electrode

Applications:
A preliminary step of distillation of sample and collection of CN^- in alkaline solution is required. The electrode responds to CN^- concentration in the range of 0.05 to 10 mg/L

Construction:
The electrode uses a solid crystalline membrane sensitive to CN^-.

Interferences:
Since the determination is made on the distillate, ordinarily interference from other ions is not expected. Lead carbonate may be added to absorbing solution if sulphides are expected in the distillate.

Calibration:
Use a series of 4 or more standards in the range of 0.025-10mg CN^-/L. Proceed from the lowest to the highest concentration while taking readings. Mix well using a magnetic stirrer. Allow at least 5 min for reaching equilibrium.

Precaution:
HCN is an extremely toxic gas. Follow all precautions as detailed in the distillation step in standard procedures. Do not word with an acidified sample is open. The standards and the samples should be at the same temperature, preferably as close to 25^0C as possible.

4.6 Use and care of electrodes

An overview of initial use, storage and recovery for ion electrodes is given in Table 2.

Table 2 : Initiation of use of ion electrodes, storage and recovery

Kind of electrode	Initiation of use	Storage	Recovery
Glass membrane	Immerse in pure water or diluted standard liquid for several hours.	Sufficiently wash in pure water, immerse in the diluted standard liquid. For long term storage wipe, dry, store in the air safely.	Wipe the glass membrane with soft cloth or sponge impregnated with neutral detergent to clean. If the electrode is used in alkali, immerse it in 1N HNO_3 for 1 – 2 hours
Crystalline solid membrane	Holding the electrode head, shake gently 1-2 times, immerse it in the diluted standard solution for about 10 min.	Wash in pure water, immerse in diluted standard liquid. For storage, wipe dry, store in air safely.	Wipe surface with cloth or absorbent wadding impregnated with ethanol to clean. If the contamination persists, gently rub the surface with soft wash-leather
Non-Crystalline solid membrane	Wipe it with tissue, immersed in the standard liquid for 10 min. If contaminated, perform the recovery treatment, immerse dilute standard liquid for 10 min.	Wash with pure water, immerse in diluted standard liquid. Wipe thoroughly, dry and store safely in air.	Drip pure water on the fine polishing paper, polish uniformly and gently. Wash thoroughly with pure water, wipe with tissues.
Liquid membrane	Holding the electrode head, shake gently 1-2 time, immerse in diluted standard solution for 10 min.	Wash with pure water, immerse in diluted standard liquid. Wipe, dry and store safely in the air.	Replenish/replace the liquid membrane according to instruction manual. Immerse in high concentration standard liquid.
Diaphragm	Set the internal liquid and diaphragm, immerse in pure water of diluted standard liquid for 10 min.	Wash with pure water, immerse in diluted standard liquid. Remove the diaphragm, discharge the internal liquid wash with pure water, dry and store safely the main body and diaphragm	Replace the contaminated / damaged diaphragm remove contamination with immersing in 1N HNO_3 . Replace the internal liquid as per instruction manual.