

Chapter - II
Experimental

2.1 Sample collection

The sampling procedures were followed as prescribed by APHA [167]. Samples of ground water and reservoir water were collected and analyzed during august 2010, December 2010, April 2011, August 2011, December 2011, April 2012, August 2012, December 2012, April 2013, August 2013, and December 2013.

Composite sampling methods were adopted for the collection of ground water. Integrated sampling procedures were adopted for the collection of water samples from reservoirs.

The samples of water were collected into well cleaned high quality polyethylene bottles of volume 1000 cm³. The polyethylene bottles were first cleaned with luke warm water. At the time of sampling the bottles are washed with the water sample, followed by collection of sample.

2.2 Sample preservation [1]

S.No	Parameter	Container	sample size in cm ³	preservation method	Holding time
1	pH	plastic	100	none	within 15 minutes
2	Electrical conductance	plastic	100	none	within 15 minutes
3	TDS	plastic	100	none	up to 7 days
4	TH	plastic	500	HNO ₃ to pH 2	6 months
5	Calcium (II)	plastic	500	HNO ₃ to pH 2	6 months
6	Magnesium (II)	plastic	500	HNO ₃ to pH 2	6 months
7	Sodium (I)	plastic	500	HNO ₃ to pH 2	6 months
8	Potassium (I)	plastic	500	HNO ₃ to pH 2	6 months
9	Iron (II)	plastic	500	HNO ₃ to pH 2	6 months
10	Chloride	plastic	100	none	28 days
11	Nitrite	plastic	100	none	48 hours
12	Fluoride	plastic	100	none	28 days
13	Phosphate	plastic	100	none	28 days
14	Total alkalinity	plastic	100	none	14 days

Table 2.2 Sample preservation

2.3 MATERIAL AND METHODS

Reagents and Chemicals

All the chemicals and reagents used were of BDH and E. Merck, Analytical Grade of purity 99.99%. For the preparation of all the reagents double distilled water was used.

Preparation of standard solutions for titrimetric analysis

a. Sulphuric acid

A solution of 1.0 mol dm^{-3} sulphuric acid is prepared by dissolving requisite concentrated sulphuric acid in 500 cm^3 and standardized with a solution of standard sodium carbonate solution using methyl orange as indicator. A solution of required dilution is prepared from such solution by proper dilution.

b. EDTA

A solution of 0.01 mol dm^{-3} EDTA is prepared by dissolving requisite amount of EDTA in 1000 cm^3 and standardized [168] with standard zinc sulphate solution.

c. Silver nitrate

A solution of 0.05 mol dm^{-3} silver nitrate is prepared by dissolving requisite amount of the substance in 1000 cm^3 and standardized [168] with a solution of standard sodium chloride using potassium chromate as indicator.

2.3.1 Preparation of stock solutions for spectrophotometric determinations

a. Iron (III)

For the determination of iron by spectrophotometer, a stock solution of iron is prepared by dissolving requisite amount of ferric ammonium sulphate in 10 cm^3 of concentrated hydrochloric acid. After complete dissolution, the solution is made up to the mark using distilled water in a 1000 cm^3 volumetric flask and standardized [168]. Such solution contains 1 mg of iron per 1 ml of solution.

b. Fluoride

A stock solution of fluoride is prepared by dissolving requisite amount of sodium fluoride in 1000 cm³ volumetric flask. From such solution further dilutions were made for analysis

c. Nitrite

A solution of nitrite is prepared by dissolving requisite amount of sodium nitrite in 1000 cm³ and standardized [168]. Appropriate dilutions were made for spectrophotometric analysis.

d. Phosphate

For the spectrophotometric determination of phosphate a solution of phosphate is prepared by dissolving requisite amount of disodium hydrogen phosphate in 1000 cm³ and standardized [168]

2.3.2 Preparation of solutions for flame-photometric determinations [168]

a. Sodium

A solution of sodium was prepared by dissolving requisite amount of sodium chloride in 1000 cm³. Required dilutions were made from such solution for analysis.

b. Potassium

A solution of sodium was prepared by dissolving requisite amount of potassium chloride in 1000 cm³. Required dilutions were made from such solution for analysis.

2.3.3 Preparation of chromomeric reagents for spectrophotometric determinations

a. Hydroxyl ammine hydrochloride

An accurately weighed quantity of 20g hydroxyl ammine hydrochloride is prepared dissolving the substance in distilled water and made up to the mark in a 100 cm³ volumetric flask.

b. 1,10-phenanthraline

A solution of 1,10 -phenanthraline is prepared by dissolving requisite quantity of the substance in 100 cm³.

c. Sodium acetate buffer

A solution of the buffer is prepared by dissolving an appropriate amount of sodium acetate in glacial acetic acid. The resulting solution is made up to the mark in a 100 cm³.

d. 1% (V/V) hydrochloric acid

A solution of 10% Hydrochloric acid is prepared by dissolving of 10 cc of concentrated hydrochloric in 100 cm³. Appropriate dilutions were made from such solution and prepared 1% hydrochloric acid solution.

e. 20% (V/V) hydrochloric acid

This solution is prepared by dilution of 20 cc of concentrated hydrochloric acid in a 100 cm³.

f. Sulphanilamide

The solution of sulphanilamide for the spectrophotometric determination of nitrite in water is prepared by dissolving requisite amount of sulphanilamide in 20% (V/V) hydrochloric acid solution in a 100 cm³.

g. NEDA

The solution of NEDA for the spectrophotometric determination of nitrite in water is prepared by dissolving requisite amount of the substance in 1% (V/V) hydrochloric acid solution in a 100 cm³

h. Alizarin red

For the spectrophotometric determination of fluoride in water, a solution of alizarin red is prepared by dissolving requisite amount of alizarin red in 100 cm³.

i. Zirconyl oxychloride

A solution of zirconyl oxychloride is prepared by dissolving requisite amount of the substance in 100 cm³.

j. Ammonium molybdate

This solution is prepared by dissolving requisite amount of ammonium molybdate in hot water. The resulting solution after cooling is made up to the mark in 100 cm³.

k. Ascorbic acid

Freshly prepared Ascorbic acid solution is used throughout the course of study. The solution is prepared by dissolving requisite amount of ascorbic acid in 100 cm³.

2.3.4 Preparation of indicators

a. Eriochrome black T

Accurately weighed amount, 0.2 g of the powdered dye stuff EBT, is transferred into a reagent bottle and dissolved by the addition of 15 cm³ of triethanolamine, followed by the addition of 5 cm³ of ethyl alcohol. Such solution is used as indicator for the complexometric determinations.

b. Murexide indicator

A pinch of murexide indicator as such in powdered form is used for analysis.

c. Methyl orange

A solution of methyl orange is prepared by dissolving requisite amount of the substance in 100 cm³.

d. Phenolphthalein

Phenolphthalein indicator solution is prepared by dissolving requisite amount of the powdered sample in 50% ethanol solution, and the resulting solution is made up to the mark in 100 cm³.

e. Potassium chromate

Potassium chromate indicator for the determination of chloride is prepared by dissolving 10.0g of potassium chromate in 100 cm³.

2.3.5 Preparation of special reagents

a. Preparation of pH-10 buffer

Accurately weighed quantity of 17.5 g of ammonium chloride is dissolved by the addition of 142 cc of liquor ammonia. The resulting solution is made up to the mark in a 250 cm³. The pH of the solution is adjusted by using a pH meter. A freshly prepared solution of pH-10 buffer was used throughout.

b. 4 mol dm⁻³ sodium hydroxide

This solution is prepared by dissolving accurately weighed quantity 80.0g of sodium hydroxide pellets in distilled water. The resulting solution is made up the mark in a volumetric flask of volume 500 cm³.

2.4. METHODOLOGY

The methodology employed for the determination of various physico- chemical parameters under study is mentioned in the table given below.

S.NO	Parameter	Method	Instrument/ equipment used
1	pH	pH-metric	pH meter
2	Electrical conductance	conductometric	Conductivity meter
3	TDS	Gravimetric	Glassware
4	TH	Complexometric titration	Glassware
5	Ca (II)	Complexometric titration	Glassware
6	Mg (II)	Complexometric titration	Glassware
7	Na(I)	Falme photometric	Falme photometer
8	K (I)	Falme photometric	Falme photometer
9	Fe (II)	Spectrophotometric	spectrophotometer
10	Chloride	Spectrophotometric	spectrophotometer
11	Phosphate	Spectrophotometric	spectrophotometer
12	Fluoride	Spectrophotometric	spectrophotometer
13	Nitrite	Spectrophotometric	spectrophotometer
14	Total alkalinity	Volumetric	Glassware
15	Heavy metals	ICP-OES	ICP-OES

Table 2.4. Experimental methodology

2.5 INSTRUMENTS USED FOR ANALYSIS WITH SPECIFICATIONS

pH of all the requisite solutions were measured by using ELICO LI 120 pH meter

ELICO CM 180 conductivity meter is used for the measurement of electrical conductivity of water samples.

Microprocessor based Flame photometer (ELCIO CL 361 model) is used for the determination of sodium and potassium in the water samples.

ELICO SL 177 spectrophotometer with matched set of cuvettes, with a range 300-1000 nm bandwidth 5 nm was used for the spectrophotometric analysis of the selected parameters.

Perkin Elmer 8X100 ICP-OES was used for the determination of heavy metals in the water samples of the study.

2.6 ANALYTICAL PROCEDURES

pH [167]

The instrument is switched on for 30 minutes to warm as per the instructions prescribed. After the predetermined time the instrument is calibrated by using standard buffer solutions of pH 4, 7 and 9.2. In a 100 cm³ beaker the sample of water for which the pH is determined is placed and the pH of the sample is measured by inserting the electrode in the sample.

Electrical conductance [167]

The instrument is switched on to warm up. By making all the necessary calibration adjustments, the sample of water is taken into a beaker of volume 100 cm³ and by inserting the conductivity cell of appropriate cell constant the electrical conductance of the sample is determined. After every measurement the conductivity cell is cleaned well with distilled water.

Total dissolved solids [167]

The sample of water previously filtered is placed in a pre-weighed crucible. The crucible along with the sample of water is heated until the last drop of water gets

evaporated. Then the crucible cooled to room temperature and weighed. The difference in the weights gives the value of TDS of the sample of water.

Total hardness

Total hardness was determined by EDTA Titrimetric method [167]. 50 cm³ of the water sample was titrated against standard EDTA (0.01mol dm⁻³) solution using Eriochrome Black T as the indicator at a pH of 10 (ammonia buffer was used). The results are expressed in ppm or mg/l calcium carbonate.

Calcium and magnesium

The total hardness value includes hardness due to calcium and magnesium ions. The titration was repeated using murexide as indicator at a pH of 12 with 4mol dm⁻³ sodium hydroxide solution. The titer value corresponds to the amount of Ca (II) in the sample. The difference between the titer value for total hardness and calcium has been used to calculate the concentration of magnesium in the sample [168]. The results are expressed in ppm or mg/L.

Total alkalinity

Total alkalinity is determined by titrating a sample of 50 cm³ of water with standard sulphuric acid using methyl orange as indicator [168]. The results are expressed as mg/L. Alkalinity due to carbonate is determined by the titration of sample of water with standard acid solution in the presence of phenolphthalein indicator.

Determination of chloride

Chloride ion in the water samples is determined by Mohr's method [168]. A sample of volume 50cm³ is titrated with standard silver nitrate solution in the presence of potassium chromate as indicator. This titration is carried out in the presence of calcium carbonate to maintain alkaline medium.

Determination of sodium and potassium

Sodium and potassium in water is determined by using Flame photometer [168]. By preparing solutions of varying concentrations of sodium (I), potassium (I) and the

corresponding detector responses are recorded. From the plot drawn by taking concentration on abscissa and the corresponding detector responses on ordinate, the concentration of sodium and potassium is obtained. To analyze the content of sodium and potassium in samples of water, the water samples is diluted with distilled water to an appropriate range.

Determination of fluoride [168]

Beer's law plot prepared by, drawing a graph by taking concentration of fluoride on abscissa and the corresponding absorbance values on ordinate. For preparing such a plot, from the stock solution series of solutions were prepared. To an aliquot of such solution zirconyl oxychloride and alizarin red solutions were mixed. And from such a plot concentration of fluoride in the sample of water is determined.

Determination of phosphate [168]

Beer's law plot prepared by, drawing a graph by taking concentration of phosphate on abscissa and the corresponding absorbance values on ordinate. For preparing such a plot, from the stock solution series of solutions were prepared. To an aliquot of such sample ammonium molybdate solution and ascorbic acid solution were mixed. Absorbance for the resulting blue color was measured at 820 nm. And from such a plot concentration of phosphate in the sample of water is determined.

Determination of nitrite [168]

Beer's law plot prepared by, drawing a graph by taking concentration of nitrite on abscissa and the corresponding absorbance values on ordinate. For preparing such a plot, from the stock solution series of solutions were prepared. To an aliquot, sulphanilamide and NEDA solutions were mixed. A reddish purple color is the resultant. Absorbance measurements were recorded at 540 nm. And from such a plot concentration of nitrite in the sample of water is determined.

Determination of iron [168]

Beer's law plot prepared by, drawing a graph by taking concentration on abscissa and the corresponding absorbance values on ordinate. For preparing such a plot, from the stock solution series of solutions were prepared. To an aliquot, sodium acetate buffer, 1, 10,- phenanthraline solution were mixed. A bright orange color is the resultant. Absorbance was measured at 520 nm. And from such a plot concentration of iron in the sample of water is determined.

Determination of heavy metals

Selected heavy metals for the analysis are performed by inductively coupled plasma method [167].