EFFECT OF COAL BASED INDUSTRIES ON SURFACE WATER QUALITY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY
IN
MINING ENGINEERING

BY
JIVITESH PATRA
Roll No.-10605011

DEPARTMENT OF MINING ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA - 769008
2010

EFFECT OF COAL BASED INDUSTRIES ON SURFACE WATER QUALITY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY
IN
MINING ENGINEERING

BY
JIVITESH PATRA
Roll No.-10605011

Under the Guidance of

Dr. H. B. SAHU
Associate Professor

DEPARTMENT OF MINING ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA - 769008
2010

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

CERTIFICATE

This is to certify that the thesis entitled **“Effect of Coal Based Industries on Surface Water Quality”** submitted by **Sri Jivitesh Patra** in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

Date:

Dr. H. B. Sahu
Associate Professor
Dept. of Mining Engineering
National Institute of Technology
Rourkela – 769008

ACKNOWLEDGEMENT

I wish to express my deep sense of gratitude and indebtedness to Dr. H. B. Sahu, Associate Professor, Department of Mining Engineering, NIT, Rourkela; for introducing the present topic and for his inspiring guidance, constructive and valuable suggestion throughout this work. His able knowledge and expert supervision with unswerving patience fathered my work at every stage, for without his warm affection and encouragement, the fulfillment of the task would have been very difficult.

I would also like to convey my sincere thanks to the faculty and staff members of Department of Mining Engineering, NIT Rourkela, for their help at different times.

I am also thankful to Dr. R.K. Patel, H.O.D., Department of Chemistry and Dr. Kakoli Karar (Paul), Assistant Professor, Department of Civil Engineering for permitting me to carry out the experiments in the Environmental Engineering Lab.

I am also thankful to Mr. B. K. Bhoi, Mr. B.N. Naik, Mr. B. K. Pradhan and Mr Soma Oram for their help in carrying out different experiments in the laboratory.

Apart from these I feel grateful and obliged to Er. S. Dash, Regional Officer and Mr. Anup Mallick, Environmental Scientist, State Pollution Control Board, Rourkela for their help in carrying out some of the experiments at their laboratory.

Last but not least, my sincere thanks to all my friends and family members who have patiently extended all sorts of help for accomplishing this project.

Date: JIVITESH PATRA

ABSTRACT

Introduction

The expected increase in the use of coal as an energy source has resulted in several investigations into environmental cycling of coal related pollutants. Among these is the release of various liquid effluents, which are associated with coal during the carbonization, cleaning and combustion processes. The coal based industries, such as by-product coke-plants, coal washeries and thermal power plants release their liquid effluents, which are needed urgent attention for the treatment, before they are discharged into the fresh water streams. There is also the release of ash pond decant into the local water bodies from the coal-based industries. Such release of ash pond decant tends to deposit ash all along its path thereby causing fugitive dust nuisance when it dries up. Also when such water mixes with a water body, it increases the turbidity of the water body thereby decreasing the primary productivity. This is harmful to the fisheries and other aquatic biota in the water body.

The objective of this project work is to analyze the environmental impacts of waste water discharged from coal based industries and need to recognize that effects are both positive and negative.

Water Quality Parameters and their Tests

Nine water samples were collected from different coal based industries, viz. NALCO, Angul; RSP, Rourkela and NTPC, Talcher. Sample collection had been carried out as per the norms laid by Central Pollution Control Board (CPCB). The water samples were collected in a clean white leak proof bottle of capacity 100 ml or 250 ml or 500 ml. Various water quality parameters were studied and their tests were carried out. Experimental investigations have been performed as per American Public Health Association (APHA). The water samples were filtered before analyzing. The various water parameters that were studied were are as follows:

1. Physical Parameters: Color, Turbidity, Odor, Total Suspended Solids, Total Dissolved Solids and Conductivity.
2. Metals: Iron, Arsenic, Lead, Aluminum, Calcium and Hardness.
3. Inorganic Non-metallic Parameters: Acidity, Alkalinity, Chloride, Fluoride, pH and Sulfate.
4. Organic Parameters: Biological Oxygen Demand, Chemical Oxygen Demand and Dissolved Oxygen

The results of different water quality parameters have been presented in table 1.

Table-1: Water Sample Results

Sl. No.	Parameter	NALCO, Angul				RSP, Rourkela			NTPC,Talcher	
		S-1	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**
1	Alkalinity (mg/l)	200	230	199	240	102	306	101.2	132	76.5
2	Ammonia (mg/l)	1	1.2	1.1	1.3	0.61	1.22	4.8	2	0.5
3	Arsenic (mg/l)	0.01	0.001	0.02	0.03	0.03	0.005	0.01	0.04	0.02
4	BOD(mg/l)	25	26	29	27	16	10	12	14	13
5	Calcium (mg/l)	70	76	73	78	28.44	18.96	47.4	37.92	28.44
6	Chloride (mg/l)	121	131	129	126	121.4	60.72	101.2	105	40.48
7	COD(mg/l)	96	74	68	56	76	64	69	62	58
8	Color(Hazen Units)	5 Hz	6 Hz	7 Hz	8 Hz	20 Hz	5 Hz	10 Hz	10 Hz	5 Hz
9	Conductivity (micro siemens)	340	330	290	270	245.4	233.9	240.8	285.1	263.7
10	Fluorides (mg/l)	1.5	1.7	1.89	2.1	3	0.5	1.5	1.5	1
11	Iron(mg/l)	3.0	2.5	3.3	3.2	1.17	0.614	0.73	1.5	1.3
12	Lead(mg/l)	0.05	0.06	0.06	0.08	0.04	0.01	0.02	0.03	0.02
13	pH	8.9	8.7	8.6	8.0	6.9	7.2	7.0	5.8	8.2
14	TSS (mg/l)	78	96	99	111	82	68	74	61	58
15	Turbidity(NTU)	12.6	13.9	14.9	13.4	21.7	4.5	4.9	6	5.5
16	TDS (mg/l)	108	112	119	110	136.1	129.4	132.5	154.9	141.3
17	Hardness mg/l)	280	278	270	265	1516.8	1279.8	1256.1	284.4	758.4
18	Sulfate (mg/l)	32	34	36	31	160	35	38	50	40

Discussion

The pH of all samples were within the limits. The turbidity of S-5 was highest among all the samples. The hardness value of S-5 was highest followed by S-6 and S-7. The BOD of S-3 and S-4 were higher in comparison to other samples. The COD values were within the limits. The ammonia content of S-7 was quite high. The iron content of S-3 and S-4 was very high and the values exceeded the prescribed limits.

Conclusion

It may be concluded that the S-3 water sample from NALCO, Angul; S-5 water sample from RSP, Rourkela and S-8 water sample from NTPC, Talcher were the most polluted water samples. The overall management is necessary and Central Pollution Control Board (CPCB)/ State Pollution Control Board (SPCB) rules should be strictly implemented. Educating the urban as well as the rural mass is one of the major step to put a check on the surface water pollution.

References

American Public Health Association (APHA),1985, Standards Methods for Examination of Water and Wastewater, 16th Edition, United States of America, Baltimore, Maryland.

Rao, C S, 1994,"Waste Water Sampling and Analysis, Chapter-8", Environmental Pollution Control Engineering, Second Edition, Willey Eastern Limited, Page: 313-328.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER

1

INTRODUCTION

NEED OF THE STUDY

OBJECTIVES OF THE STUDY

1. INTRODUCTION

Environmental impacts of waste water discharged from coal-based industries, such as by-product coke plant, coal washery and thermal power plant are numerous. The coke plant waste water contains high concentration of phenol, ammonia and cyanide, which have got detrimental effect on environment. In few coal based industries, waste water containing high concentration of coal fines is released, which creates a visible pollution in fresh water stream. A large amount of good quality coal is also lost by the washery everyday. In the thermal power plants, coal ash discharged in slurry form in the ash pond may affect the surrounding ground and surface water due to leachates generated from it.

The expected increase in the use of coal as an energy source has resulted in several investigations into environmental cycling of coal related pollutants. Among these is the release of various liquid effluents, which are associated with coal during the carbonization, cleaning and combustion processes. The coal based industries, such as by-product coke-plants, coal washeries and thermal power plants release their liquid effluents, which are needed urgent attention for the treatment, before they are discharged into the fresh water streams. In by-product coke plants, coal gas produced during coking process is cooled and cleaned by large amount of water. This generates ammoniacal liquor, which comes out as effluent.

1.1 NEED OF THE STUDY

In the thermal power plants, ash formed during combustion of coal is mixed with water and is discharged in slurry form in ash disposal ponds. If disposal ponds are not properly selected, constructed and managed and the coal ashes are not properly assessed for disposal, the risk of ground and surface water contamination due to leaching of heavy metal ions in the coal ash or surface run-off is enhanced. Due to this the ground water gets polluted and may become unsuitable for domestic use. There is also the release of ash pond decant into the local water bodies from the coal-based industries. Such release of ash pond decant tends to deposit ash all along its path thereby causing fugitive dust nuisance when it dries up. Also when such water mixes with a water body, it increases the turbidity of the water body thereby decreasing the primary productivity. This is harmful to the fisheries and other aquatic biota in the water body.

1.2 OBJECTIVES

Keeping the above problem in mind, the following objectives have been planned

- Study of Environmental impacts of waste water discharged from coal-based industries, such as by-product coke plant, coal washery and thermal power plants
- Collection of water samples from a few coal based industries.
- Analysis of water quality of the collected samples
- Assessment of environmental impact and suggestion of remedial measures

CHAPTER

2

LITERATURE REVIEW

WHY DO SURFACE WATER SUPPLIES MERIT PROTECTION

POLLUTION OF AQUIFIERS

SURFACE WATER CONTAMINANTS

HEALTH IMPACTS OF WATER POLLUTION FROM COAL-BASED INDUSTRIES

WATER QUALITY INDEX

2. LITERATURE REVIEW

Singh (1990) presented the status of water quality and its propensity in the Jharia Coalfield-where about thirty major industries (mainly large sized and coal based) exit besides extensive coal mining activities. This study revealed that water is grossly polluted in the entire coal mining area. Major sources which result water quality deterioration in the region have been accounted. Inventories of water resources and its propensity have also been established.

Tiwary and Dhar (1994) studied the water quality of the river Damodar in a stretch of 50 km in Jharia coalfield region with specific reference to heavy metals. Sediments of the river bed was characterized for heavy metals, Fe, Mn, Cd, Cr, Ni and Pb to determine total carry over of heavy metals in the river body. Heavy metal concentrations in the river sediments were higher than in the river water. The study also showed that Fe and Mn were irreversibly retained in the sediment and this effect was also observed for other metals in decreasing: Pb, Cr, Ni and Cd.

Jambrik and Bartha (1994) studied the original and secondary effects on ground water quality by mining in the East Borsod Coal Basin, Hungary. They found that in all almost all Hungarian coal basins, intensive dewatering lowers the hydrostatic pressure of aquifers, reduce their water resources, unbalance water management of the area.

Baba et. al. **(2003)** studied the the effect of Yatagan Thermal Power Plant (Mugla, Turkey) on the quality of surface and ground waters. Their study revealed that the concentrations of Ca^{2+}, Cd^{2+}, Pb^{2+}, Sb^{2+} and $SO_4{}^{2-}$ in some samples exceed the Turkish Drinking Water, the U.S. EPA and WHO limits. Isotope analyses were carried out to determine the origins of waters, which showed that contamination is taking place in the vicinity of the waste disposal site.

Erbe et. al. (2003) found that elevated concentrations of several trace elements (arsenic and manganese) and major ions (calcium, magnesium, chloride and sulfate) were found in fly ash pore water, indicating that leachate is formed within the fly ash fill. The purpose of the study was to determine the potential for leachate to form within pore water in Coal Combustion Product embankments, and evaluate whether leachate is degrading ground water quality.

Junshum et. al. (2004) studied the water quality at the Mae Moh Power Plant, Lampang Province. They conducted the monitoring of water quality from six reservoirs around Mae Moh thermal power plant were conducted during January – December 2003. There was a statistical significantly differences for values of electrical conductivity, total dissolved solid, hardness, silica, arsenic and lead between natural water sources: Mae Kham and Mae Chang reservoirs and reservoirs in wastewater treatment system: Settleable solid and Oxidation pond, Bio-treatment pond, Diversion pond and South wetland pond, which receiving the effluent from the plant.

Qian et. al. (2007) made surface water quality evaluation using multivariate methods and a new water quality index in the Indian River lagoon, Florida. Their objective was to study the water quality using several multivariate techniques and a comprehensive water quality index. Clustering was used to cluster the six monitoring stations into three groups, with stations on the same or characteristic-similar canals being in the same group.

Parashar et. al. (2007) assessed the possible impacts of climate change in water reservoir of Bhopal with special reference to heavy metals, Central region. India. Their study revealed that physico – chemical characteristics of the reservoir water largely varied through change of season, degree of anthropogenic activities in and around, the composition of runoff in the catchment area.

Bishnoi and Malik (2008) studied the systematic physico-chemical analysis of the groundwater at 41 different locations in Panipat city (Haryana), India to evaluate its suitability for domestic purposes. Their data revealed considerable variations in the water samples with respect to chemical composition and they found that all samples have high concentration of dissolved salts and all the samples were hard to very hard.

Kuipers (2008) studied the effects of coal bed methane production on surface and ground water resources. He conducted two studies to assist Northern Plains Resource Councils efforts to address CBM. The purpose of the study was the need to understand how produced water is disposed and recognize that effects are both positive and negative.

Kar et. al. **(2008)** studied the assessment of heavy water pollution in surface water. They collected a total of 96 surface water samples collected from river Ganga in West Bengal during 2004-05 was analyzed for pH, EC, Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni. They found that among the heavy metals themselves, a significant negative correlation was observed between Fe and Cr, whereas Ni exhibited a significant positive correlation with Mn and Zn.

Gendren et. al. (2009) found that ambient concentrations of metals in surface waters have become an important consideration when establishing water quality criteria and conducting risk assessments. Their study sought to estimate amounts of copper that may be released into fresh and estuarine waters considering ambient concentrations, toxicity thresholds, and bioavailability. Cumulative distribution functions of ambient copper concentrations were compared statistically for individual sites within 14 surface waters of North America and Europe to identify differences among mean distribution variables.

Tiri and Boudoukha (2010) studied the quality of water surface of Koudiat Medouar dam. Principal components analysis results revealed that surface water quality was mainly controlled by geology, agricultural uses and domestic discharges. They also found that the water is heavily influenced by geology, and by traces of metals (iron, lead), and also marked by high levels of nitrate, ammonium and sodium due to urban pollution.

Xing (2010) analyzed the water consumption actuality of the electric power industry of China and the necessity of the water-saving transformation in thermal power plants was proposed. The type of water consumption was also summarized in the production of thermal power plants. They also proposed the methods of technical reform of water conservation in the thermal power plants of China and offered solutions for the energy conservation and emission reduction.

2.1 WHY DO SURFACE WATER SUPPLIES MERIT PROTECTION?

- Surface water is a vital natural resource for the reliable and economic provision of potable water supply in both the urban and rural environment. It thus plays a fundamental role in human well-being, as well as that of some aquatic and terrestrial ecosystems.

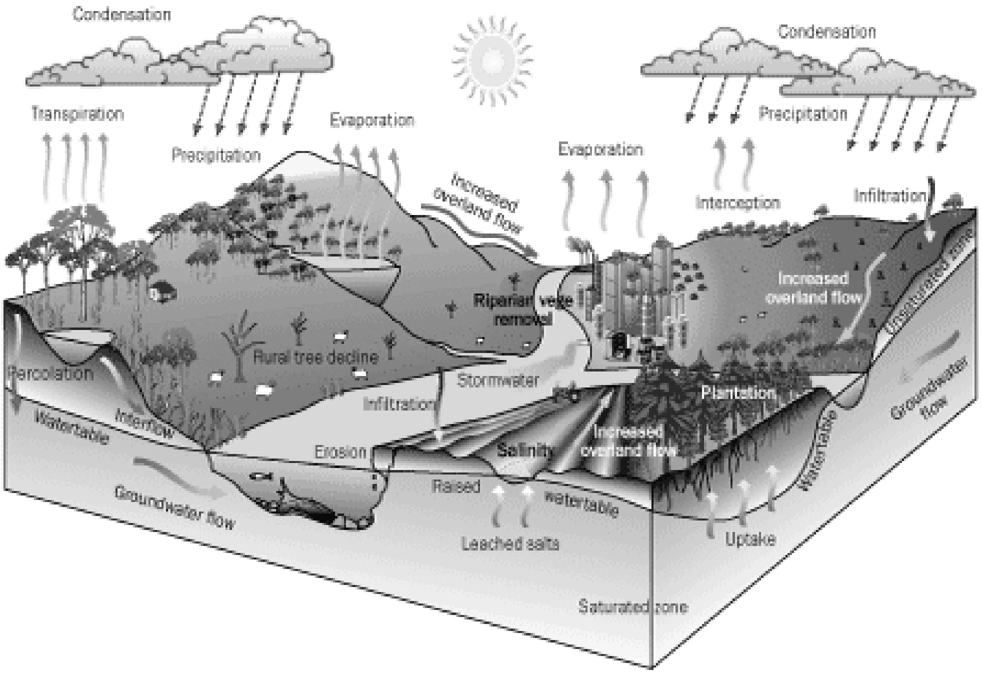

Figure 2.1: Land-use activities commonly generating a surface water pollution threat

Source: http://soer.justice.tas.gov.au/2009/image/126/ilw/o-Waterlanduse-126-m.gif

- For municipal water supply, high and stable raw-water quality is a prerequisite, and one best met by protected groundwater sources. Recourse to treatment processes (beyond precautionary disinfection) in the achievement of this end should be a last resort, because of their technical complexity and financial cost, and the operational burden they impose.
- Worldwide, aquifers (geological formations containing usable surface water resources) are experiencing an increasing threat of pollution from urbanization, industrial development, agricultural activities and mining enterprises. Thus proactive campaigns and practical actions to protect the natural (generally excellent) quality of groundwater are widely required, and can be justified on both broad environmental- sustainability and narrower economic-benefit criteria.

- In some cases it may take many years or decades before the impact of a pollution episode by a persistent contaminant becomes fully apparent in surfacewater supplies abstracted from deeper wells. This can lead to complacency over the pollution threat. But the real implication is that once groundwater quality has become obviously polluted, large volumes of aquifer are usually involved. Thus clean-up measures nearly always have a high economic cost and are often technically problematic.

2.2 HOW DO AQUIFERS BECOME POLLUTED?

- The pollution of aquifers occurs if the subsurface contaminant load generated by man-made discharges and leachates (from urban, industrial, agricultural and mining activities) is inadequately controlled, and (in certain components) exceeds the natural attenuation capacity of the underlying soils and strata (Figure 2.1).
- Natural subsoil profiles actively attenuate many water pollutants and have long been considered potentially effective for the safe disposal of human excreta and domestic wastewater.
- The auto-elimination of contaminants during subsurface transport in the vadose (or unsaturated) zone is the result of biochemical degradation and chemical reaction, but contaminant retardation (due to sorption on the surfaces of clay minerals and/or organic matter) is also of importance, since it greatly increases the time available for processes resulting in contaminant elimination.
- However, not all subsoil profiles and underlying strata are equally effective in contaminant attenuation. Concern about surface water pollution relates primarily to the so-called phreatic (unconfined) aquifers, especially where their vadose zone is thin and their water-table shallow, but may also arise even where aquifers are semi-confined, if the confining aquitards are relatively thin and permeable.
- An idea of more common types of activity capable of causing significant surface water pollution hazard can be gained from Table 1. It is important to recognize that these depart widely from activities and compounds most commonly polluting surface water bodies.
- It is also important to stress that certain industrial and agricultural practices (and specific incremental processes within such practices) often present disproportionately large

threats to groundwater quality. Thus sharply-focused and well-tuned pollution control measures can produce major benefits for relatively modest cost.

Table: 2.1-Common surface-water contaminants and associated pollution sources

Pollution source	Type of contaminant
Agricultural Activity	nitrates; ammonium; pesticides; fecal organisms
In-situ Sanitation	nitrates; fecal organisms; trace synthetic hydrocarbons
Gasoline Filling Stations and Garages	benzene; other aromatic hydrocarbons; phenols; some halogenated hydrocarbons
Solid Waste Disposal	ammonium; halogenated hydrocarbons; heavy metals
Metal Industries	trichloroethylene; tetrachloroethylene; other halogenated hydrocarbons; heavy metals; phenols
Timber Industry	pentachlorophenol; some aromatic hydrocarbons
Pesticide Manufacture	various halogenated hydrocarbons; phenols; arsenic
Sewage Sludge Disposal	nitrates; various halogenated hydrocarbons; lead; zinc
Oil and Gas Exploration/Extraction	salinity (sodium chloride); aromatic hydrocarbons
Metalliferous and Coal Mining	acidity; various heavy metals; iron; sulphates

Source: Source: http://www.lenntech.com/groundwater/pollution-sources.htm

2.3 HEALTH IMPACTS OF WATER POLLUTION FROM COAL-BASED INDUSTRIES

Arsenic: *Arsenic poisoning* interferes with cellular longevity by allosteric inhibition of an essential metabolic enzyme pyruvate dehydrogenase (PDH) complex which catalyzes the reaction Pyruvate + CoA-SH + NAD+ PDH Acetyl-Co-A + NADH + CO_2. With the enzyme inhibited, the energy system of the cell is disrupted resulting in an apoptosis episode. Arsenic in cells clearly stimulates the production of hydrogen peroxide (H_2O_2).

When the H_2O_2 reacts with Fenton metals such as iron, it produces a highly reactive hydroxyl radical. Inorganic Arsenic trioxide found in ground water particularly affects Voltage-gated potassium channels , disrupting cellular electrolytic function resulting in neurological disturbances, cardiovascular episodes such as prolonged qt interval, high blood pressure central nervous system dysfunction and death.

Lead: *Lead poisoning* (also known as plumbism, colica pictonium, saturnism, Devon colic, or painter's colic) is a medical condition caused by increased levels of the heavy metal lead in the body. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders. Symptoms include abdominal pain, headache, anemia, irritability, and in severe cases seizures, coma, and death.

Aluminum: Aluminum Toxicity is particularly poisonous to the nervous system with a range of symptoms that can include disturbed sleep, nervousness, emotional instability, memory loss, headaches, and impaired intellect. It can stop the body's ability to digest and make use of calcium, phosphorus and fluoride. This prevents bone growth and reduces bone density. Aluminum can also cause conditions which actually force calcium out of the bones. Either of these situations can bring on weakness and deformation in the bone structure with crippling effects. Toxicity can also result in aching muscles, speech problems, anemia, digestive problems, lowered liver function, colic and impaired kidney function.

Cadmium: Cadmium is highly toxic and has been implicated in some cases of poisoning through food. Minute quantities of cadmium are suspected of being responsible for adverse changes in arteries of human kidneys. Cadmium also causes generalized cancers in laboratory animals and has been linked epidemiologically with certain human cancers. Cadmium may enter water as a result of industrialized discharges or the deterioration of galvanized pipe.

Iron: The excess iron affects organ function, presumably by direct toxic effect. Excessive iron stores exceed the body's capacity to chelate iron, and free iron accumulates. This unbound iron promotes free radical formation in cells, resulting in membrane lipid peroxidation and cellular injury.

Cyanide: Cyanide makes the cells of an organism unable to use oxygen, primarily through the inhibition of cytochrome c oxidase. Inhalation of high concentrations of cyanide causes a coma with seizures, apnea and cardiac arrest, with death following in a matter of minutes. At lower doses, loss of consciousness may be preceded by general weakness, giddiness, headaches, vertigo, confusion, and perceived difficulty in breathing. At first stages of unconsciousness, breathing is often sufficient, although the state of the victim progresses towards a deep coma, sometimes accompanied by pulmonary edema, and finally cardiac arrest.

Chromium: The hazards associated with chromium are wholly dependent upon which form of chromium is present:

a) Chromium Metal / Cr^0

Appearance: metallic grey/silver in colour

Presence: Cr plated articles, Cr present in stainless steel

Health, Safety and Environmental Effects: Essentially inert

b) Trivalent Chromium / Cr^{3+} / Cr (III)

Presence: Cr (III) plating solutions, Cr (III) passivating solutions

Health, Safety and Environmental Effects:

- Not classified as hazardous for supply
- An essential dietary element

c) Hexavalent Chromium / Cr^{6+} / Cr (VI)

Appearance: red, orange or yellow in color (dependent on specific chemical compound and concentration - most concentrated = red, least concentrated = yellow)

Presence: chromic acid, Cr (VI) plating solutions, Cr (VI) passivating, anodizing and etching solutions

Fluoride: A fluoride concentration of approx. 1mg/l in drinking water effectively reduces dental caries without harmful effects on health. Accurate determination of fluoride has increased in importance with the growth of the practice of fluoridation of water supplies as a public health measure. Maintenance of an optimal fluoride concentration is essential in maintaining effectiveness and safety of the fluoridation procedure. In high concentrations, soluble fluoride salts are toxic and skin or eye contact with high concentrations of many fluoride salts is dangerous.

2.4 WATER QUALITY INDEX

The main objective of Water Quality Index is to turn complex water quality data into information that is understandable and useable by the public. Water Quality Index based on some very important parameters can provide a simple indicator of water quality. It gives the public a general idea of the possible problems with water in a particular region.

The indices are among the most effective ways to communicate the information on water quality trends to the public or to the policy makers and water quality management. It is also defined as a rating reflecting the composite influence of different water quality parameters on the overall quality of water.

The WQI consists of nine tests:

- Dissolved Oxygen
- Fecal Coliform
- pH
- BOD (Biochemical Oxygen Demand)
- Temperature
- Total Phosphate
- Nitrates
- Turbidity
- Total Solids

2.4.1 Canadian Water Quality Index (CWQI) Equation

The index equation is based on the water quality index (WQI) endorsed by the Canadian Council of Ministers of the Environment (CCME, 2001). The index allows measurements of the frequency and extent to which parameters exceed their respective guidelines at each monitoring station. Therefore, the index reflects the quality of water for both health and acceptability, as set by the World Health Organization. The index is determined on an annual basis resulting in an overall rating for each station per year. This will allow both spatial and temporal assessment of global water quality to be undertaken.

The CWQI equation is calculated using three factors as follows:

$$\text{WQI} = 100 - \{(F_1^2 + F_2^2 + F_3^2)^{1/2} / 1.732\}$$

F_1 represents Scope: The percentage of parameters that exceed the guideline

$$F_1 = (\#\text{failed parameters} / \text{Total \# of parameters}) \times 100$$

F_2 represents Frequency: The percentage of individual tests within each parameter that exceeded the guideline

$$F_2 = (\#\text{failed tests} / \text{Total \# of tests}) \times 100$$

F_3 represents Amplitude: The extent (excursion) to which the failed test exceeds the guideline. This is calculated in three stages. First, the excursion is calculated

$$\text{Excursion} = (\text{failed test value} / \text{guideline value}) - 1$$

Second, the normalized sum of excursions (nse) is calculated as follows:

$$\text{nse} = (\sum \text{excursion} / \text{total \# of tests})$$

F_3 is then calculated using a formula that scales the nse to range between 1 and 100:

$$F_3 = \{\text{nse} / (0.01\text{nse} + 0.01)\}$$

2.4.2 WQI Designations

The index equation generates a number between 1 and 100, with 1 being the poorest and 100 indicating the best water quality. Within this range, designations have been set by CCME (2005) to classify water quality as poor, marginal, fair, good or excellent.

Table 2.2: WQI Designations

Designation	Index Value	Description
Excellent	95-100	All measurements are within objectives virtually all of the time.
Good	80-94	Conditions rarely depart from natural or desirable levels.
Fair	65-79	Conditions sometimes depart from natural or desirable levels.
Marginal	45-64	Conditions often depart from natural or desirable levels.
Poor	0-44	Conditions usually depart from natural or desirable levels.

Source: CCME Water Quality Index 1.0 Technical Report

CHAPTER

3

SAMPLING

GENERAL ASPECTS OF SAMPLING AND SAMPLE HANDLING

SAMPLE COLLECTION PROCEDURE

3. SAMPLING

3.1 GENERAL ASPECTS OF SAMPLING AND SAMPLE HANDLING

The following points should be kept in mind while collecting water samples (Nollet, 2007):

i. Initial Considerations:

Firstly, the situation to be assessed must be clearly defined. Then an appropriate sampling design should be chosen on the basis of temporal and spatial processes of the part of the ecosystem under investigation. Handling, preservation and storage of the samples should be adapted to the properties of the chemicals of interest and the effort invested should be optimized in order to obtain the necessary information with such resources are available.

ii. Spatial Aspects:

Currents in flowing water and marine eco systems must be considered. Very often stratification crucially affects the distribution of substances of interest, especially in lakes. The chosen locations or environmental sampling must be related to the expected sources of contamination, e.g., different distances downstream of a sewage effluent discharge point. A detailed description and understanding of the exact sampling site (locational coordinates, longitudinal, lateral depth, gradient, water level and distance to possible sources of contamination) is a basic requirement of designing an adequate sampling program.

iii. Temporal Aspects:

The temporal pattern of sampling is of great importance if the environment to be sampled shows change over time, e.g. river systems within minutes or hours, or lakes within days or weeks. The schedule of the sampling program depends mainly on the expected temporal resolution of changes in the environment. If many samples are taken over a period of time, it is often appropriate to match the sampling rate to the expected pattern of variation in environment.

If sampling is *time proportional*, then samples containing identical volumes are taken at constant time intervals.

In *discharge-proportional sampling* the time intervals are constant but the volume of each sample is proportional to the volume of discharge during specific time interval.

In *quantity-proportional sampling* the volume of each sample is constant but the temporal resolution of sampling is proportional to discharge.

iv. Number of Samples:

The number of samples required depends on the problem to be addressed. If an average concentration is to be obtained from several samples, a general calculation of the necessary number of samples. If peak concentrations are to be quantified, the number of samples depends on the specific problem.

v. Sample Volume:

The appropriate sample volume depends on the elements or substances required to be analyzed on their expected concentration in the sample. For trace metal analyses sample volumes of about 100 ml are sufficient in most cases. For the analysis of organic chemicals 1 L samples are commonly used. A 3 L sample volume has been suggested for both first-flush and flow-weighted composite samples in the monitoring of storm water runoff from industries and municipalities.

vi. Storage and Conservation:

Samples that are not analyzed immediately must be protected from addition of contaminants, loss of determinants by sorption or other means, and any other unintended changes that effect the concentrations of determinants of interest. For this purpose, sample bottles should be chosen for long-term storage with no or as few changes to sample compositions as possible.

- *Contamination*

An unintended contamination of samples can occur during the sampling process, either from external sources or from contaminated sampling or storage equipment. Normally, polyethylene or Teflon bottles are used in inorganic, and glass or quartz bottles in organic trace analysis.

- *Loss*

Loss during storage can result from biological purposes, hydrolysis or evaporation. Available procedures to reduce or prevent these loss processes include:

a. Acidification to pH between 1 and 2: prevention of metabolism by microorganisms and of hydrolysis and precipitation;
b. Cooling and freezing: reduction of bacterial activity;
c. Addition of complexing substances: reduction of evaporation;

d. UV radiation: destruction of biological and organic compounds to prevent complexation reactions.

- *Sorption*

Sorption to the walls of sample bottles can reduce the concentration in the water phase considerably. Depending on the target substances, plastic or quartz bottles show the lowest adsorption and can, therefore, be used for the storage of samples in aqueous solution. In general, the wall material of storage bottles can change over time and the potential for adsorption of target substances can increase considerably. In the case of many metals, this problem can be reduced by acidifying the sample.

3.2 SAMPLE COLLECTION PROCEDURE

The three places from which samples were collected are-

I. NALCO, Angul

National Aluminum Company Ltd. (NALCO) is considered to be a turning point in the history of Indian Aluminum Industry. In a major leap forward, Nalco has not only addressed the need for self-sufficiency in aluminum, but also given the country a technological edge in producing this strategic metal to the best of world standards. Nalco was incorporated in 1981 in the Public Sector, to exploit a part of the large deposits of bauxite discovered in the East Coast. Samples were collected from four locations of the Nalco ash pond. (Figure 3.1)

Figure 3.1: Location of Nalco Ash Pond, CPP, Angul

II. Rourkela Steel Plant, Rourkela

Rourkela Steel Plant (RSP), the first integrated steel plant in the public sector in India, was set up with German collaboration with an installed capacity of 1 million tonnes. It is located in the north-western tip of Orissa and at the heart of a rich mineral belt. Samples were collected from three locations of the NSPCL, Ash Dyke, RSP, Rourkela. Samples were collected from three locations of RSP, Rourkela (Figure 3.2).

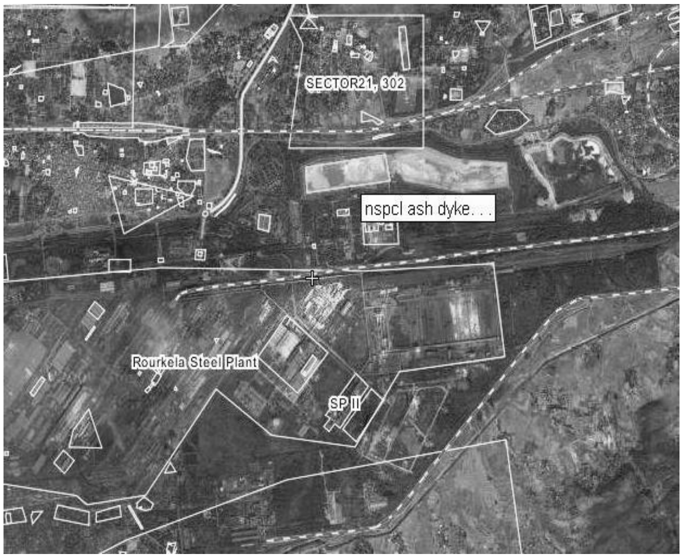

Figure 3.2: Location of NSPCL Ash Dyke, Rourkela Steel Plant, Rourkela

III. NTPC, Talcher

NTPC, India's largest power company, was set up in 1975 to accelerate power development in India. It is emerging as an’ Integrated Power Major’, with a significant presence in the entire value chain of power generation business. It has two major Power units in Orissa and both of these are situated in the district of Angul at Kaniha and Talcher. Samples were collected from two locations of NTPC, Talcher (Figure 3.3).

Figure 3.3: Location of NTPC/TTPS, Talcher

The following procedure was followed to collect the water samples from the aforementioned locations:

1. The source from where the water was collected was in regular use. Before sampling, the source was adequately flushed.
2. For hand pump sources, before collecting the water, the water was pumped and washed for at least three to five minutes to clear all dirt, turbidity and slime.
3. Water from wells was taken in the middle at mid depth. For lakes, rivers and dams, the water was near the off-take point.
4. The water was collected after clearing the suspended and floating matter.
5. Water for chemical examination was collected in a clean white plastic leak proof bottle of capacity 100 ml or 250 ml or 500 ml.
6. Before collection of sample, the container was washed/rinsed with the water to be sampled at least two or three times.
7. The water was then filled completely in the container without leaving any air space.
8. A polythene sheet (10 x 10 cm) over the cap was placed and tied with a rubber band to avoid any leak.
9. ‘The field code number (sample ID)’ was written in the container.
10. The field code number and the source details were separately recorded in a notebook.

CHAPTER

4

WATER QUALITY TESTS

PHYSICAL PARAMETERS

METALS

INORGANIC NON-METALLIC PARAMETERS

ORGANIC PARAMETERS

RESULTS

4. WATER QUALITY TESTS

Water quality is the physical, chemical and biological characteristics of water. It is most commonly used by reference to a set of standards against which compliance can be assessed. The most common standards used to assess water quality relate to drinking water, safety of human contact and for the health of ecosystems. In the present work, all the parameters were determined by using the standards prescribed by the American Public Health Association (APHA, 1985).

The water quality test is broadly divided into four parameters:

I. Physical Parameters:

This deals primarily with measurement of the physical properties of a sample. Many of the determinations included here are color, turbidity, conductivity, solids and temperature.

II. Metals:

The effect of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essential; others may adversely affect water consumers, waste water treatment systems and receiving waters. Some metals may be either beneficial or toxic, depending on their concentrations.

III. Inorganic Nonmetallic Constituents:

The measurements included in this part range from collective measurements such as acidity and alkalinity to specific analyses for individual components such as various forms of chlorine, nitrogen and phosphorous. The measurements are conducted for assessment and control of portable and receiving water quality and for determining process efficiency in water treatment.

IV. Organic Constituents:

The analysis of organic matter in water and waste water can be classified into two general types of measurements: those that seek to express either the total amount of organic matter or some fraction of the total in general terms and those that are specific for individual organic compounds.

4.1 PHYSICAL PARAMETERS

The physical parameters include

1. Color
2. Turbidity
3. Conductivity
4. Solids
5. Odor
6. Temperature

4.1.1 COLOR:

Theory

Color in water may result from the presence of natural metallic ions, humus and peat materials, plankton, weeds and industrial wastes. Color is removed to make water suitable for general and industrial applications.

Methods

- I. Visual Comparison Method
- II. Spectrophotometric Method
- III. Tristimulus Filter Method

Visual Comparison Method

Principle

Color is determined by visual comparison of a sample with known concentrations of platinum-cobalt standard solutions. Comparison also may be made with special properly calibrated glass color disks. The unit of color is defined as that produced by 1 mg/L platinum in the form of the chloroplatinate ion.

Application

This method is useful for determination of color due to naturally occurring materials, but is not applicable to most highly colored industrial wastewaters. True color is defined as color from a filtered sample, in which turbidity and suspended matter has been removed. Apparent color is that of an untreated sample and includes color due to substances in solution as well as suspended material.

Interferences

a. Turbidity results in high color values, and must be removed by filtration for determination of true color.

b. Color is extremely pH dependent and increases with increasing pH. pH of the sample at time of analysis should be reported with color data. When reporting a color value, specify the pH at which color is determined.

Apparatus

i. Nessler tubes, matched – 50 mL low form
ii. Filtration system
- filter funnel
- filter stage
- filter barrel
- clamps
- Erlenmeyer filter flask

iii. Graduated cylinder
iv. GF/F or GF/C filter papers
v. Stainless steel screen with 1 mm^2 mesh
vi. Vacuum system and connecting hoses

Procedure

a) Add 50.0 mL of standard or sample to labeled Nessler's tubes.
b) Observe the color of each sample in comparison to the standard gradient. Look vertically down, through the tubes towards a white or specular surface placed at such an angle that light is reflected upward through the columns of water.
c) Record the color value of the nearest matching standard for each sample. Note as true color for filtered samples, and apparent color for unfiltered samples.

d) If the sample color exceeds 70 units, dilute sample to 50 mL with enough DI water to bring color within standard range.
e) Record volume of sample added.
f) Correct color value for the dilution.
g) Analyze samples quickly to minimize bacterial activity which may results in alteration of color.

Calculation

$$\text{Color units (CU)} = A \times 50/B$$

where

A: estimated color of diluted sample
B: ml sample taken for dilution

Report color results in whole numbers and record as follows:

Color	***Record to Nearest***
1-50	1
51-100	5
101-250	10
251-500	20

4.1.2 Turbidity

Theory

Turbidity is the cloudiness or haziness of a fluid caused by individual particles (suspended solids) that are generally invisible to the naked eye, similar to smoke in air. The measurement of turbidity is a key test of water quality.

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted. Turbidity measures water clarity, which allows sunlight to penetrate to a greater depth.

Turbidity in open water may be caused by growth of phytoplankton. Human activities that disturb land, such as construction, can lead to high sediment levels entering water bodies during rain storms, due to storm water runoff, and create turbid conditions. Urbanized areas contribute large amounts of turbidity to nearby waters, through storm-water pollution from paved surfaces such as roads, bridges and parking lots. Certain industries such as quarrying, mining and coal recovery can generate very high levels of turbidity from colloidal rock particles.

Methods

I. Nephelometric Method-Nephelometric Turbidity Units (NTU)
II. Visual method- Jackson Turbidity Units (JTU)

Nephelometric Method-Nephelometric Turbidity Units (NTU)

Principle

The method is based upon a comparison of the intensity of light scattered by the sample at 90 degrees to the beam path, with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. The transmitted beam is used as a reference beam to correct for small amounts of color, if present in the sample. A primary standard suspension is used to calibrate the instrument. A secondary standard suspension is used as a daily calibration check and is monitored periodically for deterioration using a primary standard.

Application

This method is very widely used because of its greater precision, sensitivity, and applicability over a wide range. The candle turbidmeter, with a lower limit of 25 turbidity units, has its principal usefulness in examining highly turbid waters. The bottle standards offer a practical means for checking raw and conditioned water at various stages of treatment process.

Interferences

i. The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles can cause high readings.
ii. The presence of true color, that is the color of water which is due to dissolved substances that absorb light, will cause turbidities to be low

Apparatus

a) Thermo Scientific Orion AQUAfast Turbidimeter
b) Silicon Oil and Polishing Cloth Kit
c) Replacement Measuring Vials
d) Glassware. Class A volumetric flasks and pipettes as required.

Procedure

a. Select “EPA 180” as the measurement mode.
b. Place the sample in a clean, dry turbidity vial. Cap securely. Wipe off excess liquid or fingerprints with a soft cloth.
c. Place into the AQ4500 sample chamber and cover with vial cap.
d. Press MEASURE key. The result will be displayed on the instrument, and can be printed out for future use. If the result is less than 40 NTU, repeat procedure for the next sample.
e. If the result is greater than 40 NTU, dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor.

Calculation

$$\text{Nephelometric Turbidity Units (NTU)} = A \times (B+C)/C$$

A: NTU found in diluted sample
B: volume of dilution water, ml
C: sample volume taken for dilution, ml

Interpretation of Results

Turbidity range (NTU)	***Nearest NTU***
0-1	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
> 1000	100

4.1.3 Conductivity

Theory

Conductivity is a the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, their total concentration, mobility, valence and temperature. The conductivity is temperature dependent and increases approximately 2% per degree in aqueous solutions for most ion.

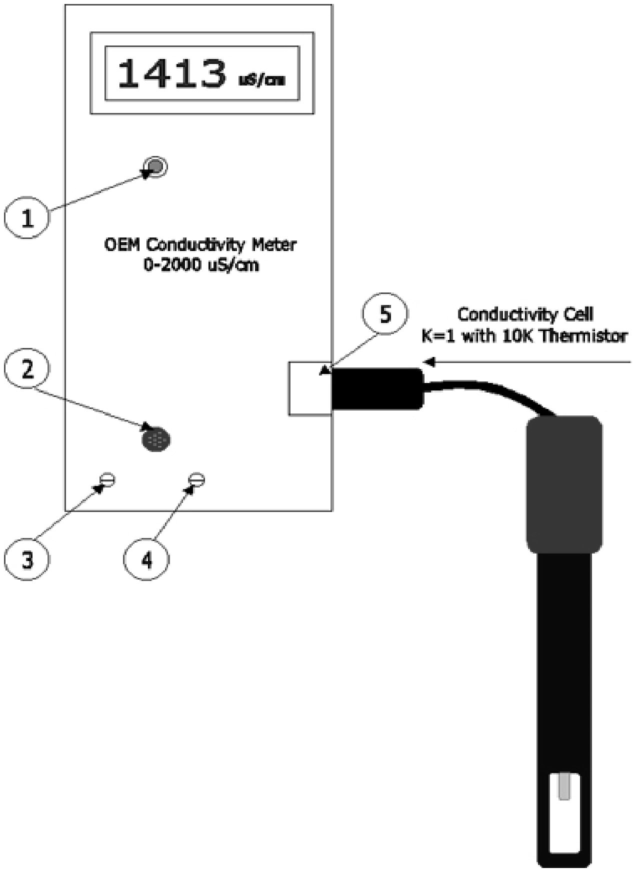

Figure 4.1: OEM Conductivity Meter

1. 0-200 uS/cm fine adjustment
2. range select:
   - 0-200 µS/cm
   - 0-2000 µS/cm
   - 0-7 µS/cm
3. 0-2000 µS/cm fine adjustment
4. Multi-positions power switch
5. LED power indicator

Procedure

A. Determination of Cell Constant

Principle

Conductance is the reciprocal of resistance in a solution and the conductivity the inverse of specific resistance. Conductivity is measured with a bridge and a measuring cell, and it is dependent upon distance between the electrodes and their area, in the measurement cell. This is expressed by the cell constant, which is a characteristic of the measurement cell.

The resistance, R, can be expressed as

$$R = \rho \frac{l}{A}$$

where

l is distance (in metres) between the electrodes and A their area (m^2).

ρ is the specific resistivity.

The specific conductance or conductivity κ is

$$\kappa = \frac{l}{\rho} \text{ or } \frac{1}{R} \cdot \frac{l}{A}$$

where $\frac{l}{A}$ is the cell constant.

Temperature Coefficient of Electrical Conductivity

The temperature coefficient of conductivity is given by the equation

$$\alpha_{\theta,25} = \frac{1}{\kappa_{25}} \left(\frac{\kappa_\theta - \kappa_{25}}{\theta - 25} \right) \times 100$$

where 25 and θ°C are the temperatures at which the electrical conductivities κ_{25} and κ_θ respectively were measured.

In order to make comparisons, it is essential that measurements are corrected to a chosen reference temperature, usually 25°C, even if the temperature of the water sample differs only slightly from that temperature.

Conversions to the electrical conductivity at 25 °C, κ_{25}, can be made using the equation

$$\kappa_{25} = \frac{\kappa_\theta}{1+ \alpha/100 \quad \theta - 25}$$

B. Instrumentation

The conductivity meter applied should have a measurement range 1–1000 µS/cm, a precision within this range of 0.5% and an accuracy within 1%. Conductivity meters may be able to give the result at a pre-selected reference temperature while the actual measurement is carried out at room temperature. Other meters need a water-bath for the measurement cell in order to give a result at 25 °C, which is the temperature used for EMEP's and WMO GAW's conductivity measurements. Besides the conductivity meter itself, a platinum conductivity cell is needed, and possibly a water bath and a thermometer.

Chemicals

i. Deionized water, conductivity < 0.5 µS/cm
ii. Potassium chloride p.a. quality

Calibration Solutions

0.1M KCl stock solution

Transfer 7.4560 g KCl, dried at least 2 hours at 110°C, to a volumetric flask and dilute to 1000.0 ml with deionized water. The solution should be transferred to a plastic flask. The stability of the solution is one year at most. A series of calibration solutions based on the 0.1 M KCl stock solution is used for the calibration procedure, as seen from Table 4.1.

Table 4.1: Calibration standards for conductivity at 25°C.

Solution	Concentration M KCl	Conductivity µS/cm	Upper limit µS/cm	Lower limit µS/cm
A	0.0500	6668	6801	6535
B	0.0200	2767	2822	2711
C	0.0100	1413	1441	1395
D	0.0050	717.8	735	700
E	0.0010	147.0	149	145
F	0.0005	73.9	77.8	70.2
G	0.0001	14.94	16.5	13.5

Calibration of the Instrument

i. *Calibration of the Cell Constant*

The cell constant should be calibrated whenever the conductivity of the 0.0010 M KCl calibration solution is outside the upper and lower limits given in Table 4.1. The age of the calibration solution must be checked before the calibration. Enter the new constant after having followed the cell constant calibration procedure given in the instrument manual. Reference temperature (or measurement temperature) should be 25°C.

ii. *Calibration with calibration solutions*

Before running a series of precipitation samples, measurements should be carried out with the 0.0001, 0.001 and 0.0100 M KCl calibration solutions. Check the age of the calibration solutions. Reference temperature should be 25°C.

Calculation

$$C = (0.001413)\ (R)\ [1+0.00191(t-25)]$$

where,

C: cell constant, cm^{-1}
R: measured résistance, ohms
t: observed temperature, C

Conductivity was determined using the following relation

$$k = (1000000)\ (C) / R\ [1+ 0.0191\ (t-25)]$$

Where

k: conductivity, µmhos/cm
t: temperature of measurement

4.1.4 Solids

Theory

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

‘‘Total solids’’ is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature.

Total solids = Total suspended solids + Total dissolved solids

‘‘Dissolved solids’’ is the portion of solids that passes through a filter of 2.0 mm (or smaller) nominal pore size under specified conditions. ‘‘Suspended solids’’ is the portion retained on the filter.

Factors affecting separation of suspended from dissolved solids:

- The type of filter holder
- the pore size
- area and thickness of the filter
- the physical nature, particle size, and amount of material deposited on the filter

4.1.4.1 Total Dissolved Solids

Total Dissolved Solids (often abbreviated TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal sol) suspended form.

Primary sources for TDS in receiving waters are agricultural and residential runoff, leaching of soil contamination and point source water pollution discharge from industrial or sewage treatment plants. The most common chemical constituents are calcium, phosphates, nitrates, sodium, potassium and chloride, which are found in nutrient runoff, general stormwater runoff and runoff from snowy climates where road de-icing salts are applied.

Principle

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

Interferences

Highly mineralized waters with a considerable calcium, magnesium, chloride, sulfate content may be hygroscopic and require prolonged drying, proper desiccation and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water trapping crust, limit sample to no more than 200 mg residue.

Figure 4.2: TDS Meter

Apparatus

a) Glass- fibre filter disks
b) Filtration apparatus

c) Gooch crucible
d) Suction flask
e) Drying oven

Calculation

Total Dissolved Solids (mg/l) = (A – B) x 1000/sample vol.(ml)

A: weight of dried residue + dish (mg)
B: weight of dish (mg)

4.1.4.2 Total Suspended Solids

Principle

A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume. To obtain an estimate of total suspended solids, calculate the difference between total dissolved solids and total solids.

Interferences

Exclude large floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that their inclusion is not representative. Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved material.

Procedure

a. *Preparation of glass-fiber filter disk:*

If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up in filtration apparatus. Apply vacuum and wash disk with three successive 20-mL portions of reagent-grade water. Continue suction to remove all traces of water, turn vacuum off, and discard washings. Remove filter from filtration apparatus and transfer to an inert aluminum weighing dish. If a Gooch crucible is used, remove crucible and filter combination. Dry in an oven at 103 to 105°C for 1 h. If volatile solids are to be measured, ignite at 550°C for 15 min in a muffle furnace. Cool in desiccator to balance temperature and weigh. Repeat cycle of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less. Store in desiccator until needed.

b. *Selection of filter and sample sizes:*

Choose sample volume to yield between 2.5 and 200 mg dried residue. If volume filtered fails to meet minimum yield, increase sample volume up to 1 L. If complete filtration takes more than 10 min, increase filter diameter or decrease sample volume.

c. *Sample analysis:*

Assemble filtering apparatus and filter and begin suction. Wet filter with a small volume of reagent-grade water to seat it. Stir sample with a magnetic stirrer at a speed to shear larger particles, if practical, to obtain a more uniform (preferably homogeneous) particle size. Centrifugal force may separate particles by size and density, resulting in poor precision when point of sample withdrawal is varied. While stirring, pipet a measured volume onto the seated glass-fiber filter. For homogeneous samples, pipet from the approximate midpoint of container but not in vortex. Choose a point both middepth and midway between wall and vortex. Wash filter with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Samples with high dissolved solids may require additional washings. Carefully remove filter from filtration apparatus and transfer to an aluminum weighing dish as a support.

Calculation

$$\text{Total Suspended Solids (mg/l)} = (A - B) \times 1000/\text{sample vol. (ml)}$$

A: weight of filter + dried residue (mg)

B: weight of filter (mg)

4.1.5 Experimental Results of Physical Parameters in Water Samples

The results of the water quality tests of the physical parameters in water samples have been presented in Table 4.2. The corresponding Indian Standards (as per E.P. Rules, 1986, Schedule VI, Standards Prescribed by SPCBs) are also given in the table.

Table 4.2: Experimental Results of Physical Parameters in Water Samples

Sl. No.	Parameters	NALCO, Angul				RSP, Rourkela			NTPC,Talcher		Indian Standards (mg/l)
		S-1	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	
1	Color(Hz)	5 Hz	6 Hz	7 Hz	8 Hz	20 Hz	5 Hz	10 Hz	10 Hz	5 Hz	25 Hz
2	Turbidity (NTU)	12.6	13.9	14.9	13.4	21.7	4.5	4.9	6	5.5	10
3	Conductivity (micro Siemens)	340	330	290	270	245.4	233.9	240.8	285.1	263.7	300
4	Total Dissolved Solids(mg/l)	108	112	119	110	136.1	129.4	132.5	154.9	141.3	500
5	Total Suspended Solids(mg/l)	78	96	99	111	82	68	74	61	58	100
6	Odor	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	-

4.2 METALS

The metals include

1. Iron
2. Arenic
3. Lead
4. Calcium
5. Hardness

4.2.1 Iron

Theory

In water samples iron may occur in true solution, in a colloidal state that may be peptized by organic matter, in inorganic or organic matter, or in relatively coarse suspended particles. In filtered samples of oxygenated surface waters iron concentrations seldom reach 1mg/l.

The excess iron affects organ function, presumably by direct toxic effect. Excessive iron stores exceed the body's capacity to chelate iron, and free iron accumulates. This unbound iron promotes free radical formation in cells, resulting in membrane lipid peroxidation and cellular injury.

Methods

I. Atomic Absorption Spectrometric Method
II. Phenanthroline Method
III. Titration Method

Titration Method

Principle

Iron sample is reduced by $SnCl_2$ to Fe^{+2} state. The Fe^{+2} is titrated by standard $KMnO_4$ solution.

$$MnO_4^{-1} + 8\,H^{+} + 5e \longrightarrow Mn^{+2} + 4H_2O$$

$$Fe^{+2} - e \longrightarrow Fe^{+3} \quad * 5$$

$$MnO_4^{-1} + 5Fe^{+2} + 8H^{+} \longrightarrow Mn^{+2} + 5Fe^{+3} + 4\,H_2O$$

$KMnO_4$ acts as self indicator and the end point is indicated by the appearance of a light pink color.

Calculation

A. Standardization of $KMnO_4$

$$S'V' = S''V''$$

$$\text{or, } S'' = S'V'/V''$$

S’: strength of oxalic acid (1.05 N/10)
V’: volume of oxalic acid (10 cc)
S”: strength of $KMnO_4$
V”: volume of $KMnO_4$

B. Iron Content

$$1000\text{ml of }1\text{N } KMnO_4 = 55.8\text{gm Fe}$$

$$X \text{ ml } S'' \; KMnO_4 = 55.8 * X * S''/1000 = w \text{ gm}$$

$$1000 \text{ ml of Iron solution contain} = w * 1000 \text{ gm/l}$$

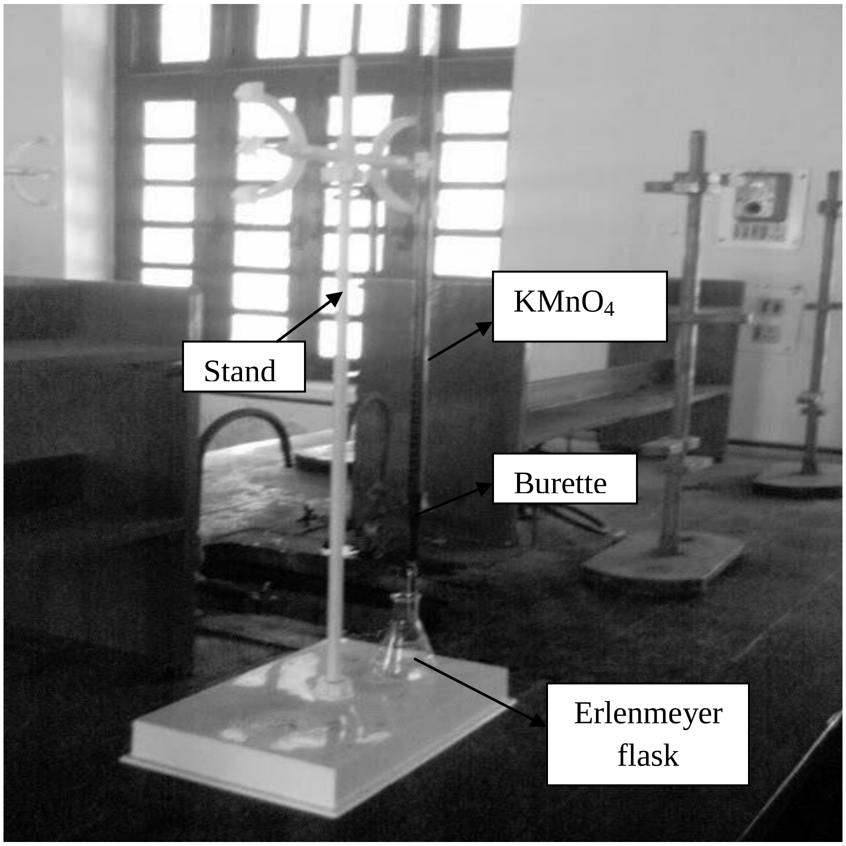

Figure 4.3: Titration Method of Iron

4.2.2 Arsenic

Theory

Arsenic may occur in water as a result of mineral dissolution, industrial discharges, or the application of industries. Severe poisoning can arise from the ingestion of as little as 100mg arsenic; chronic effects can appear from its accumulation in the body at low intake levels. Arsenic and its compounds are reported to be carcinogenic, mutagenic and teratogenic in nature.

In excessive amounts, arsenic causes gastrointestinal damage and cardiac damage. Chronic doses can cause vascular disorders such as black foot diseases.

Arsenic Poisoning

Arsenic poisoning interferes with cellular longevity by allosteric inhibition of an essential metabolic enzyme pyruvate dehydrogenase (PDH) complex which catalyzes the reaction Pyruvate + CoA-SH + NAD+ PDH Acetyl-Co-A + NADH + CO_2. With the enzyme inhibited, the energy system of the cell is disrupted resulting in an apoptosis episode. Arsenic in cells clearly stimulates the production of hydrogen peroxide (H_2O_2).

When the H_2O_2 reacts with Fenton metals such as iron, it produces a highly reactive hydroxyl radical. Inorganic Arsenic trioxide found in ground water particularly affects Voltage-gated potassium channels , disrupting cellular electrolytic function resulting in neurological disturbances, cardiovascular episodes such as prolonged qt interval, high blood pressure central nervous system dysfunction and death.

Methods:

I. Atomic Absorption Spectrometric Method

The atomic absorption spectrometric method, which converts arsenic to its hydride and uses an argon-hydrogen flame, is the method of choice.

II. Silver Diethyldithiocarbamate Method

The silver diethyldithiocarbamate method is applicable when interferences are absent.

III. Mercuric Bromide Stain Method

The mercuric bromide stain method requires care and experience and is suitable only for qualitative or semiquantitaive determinations.

4.2.3 Lead

Theory

Lead is a serious cumulative body poison. Lead in a water supply come from industrial, mine, and smelter discharges or from the dissolution of old lead plumbing.

Tap waters that are soft, acid and not suitably treated may contain lead resulting from an attack on lead service pipes. Natural waters seldom contain more than 20 µg/L, although values as high as 400 µg/L have been reported.

Lead Poisoning

Lead poisoning (also known as plumbism, colica pictonium, saturnism, Devon colic, or painter's colic) is a medical condition caused by increased levels of the heavy metal lead in the body. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders. Symptoms include abdominal pain, headache, anemia, irritability, and in severe cases seizures, coma, and death.

Routes of exposure to lead include contaminated air, water, soil, food, and consumer products.

Lead from the atmosphere or soil can end up in groundwater and surface water. It is also potentially in drinking water, e.g. from plumbing and fixtures that are either made of lead or have lead solder. Since acidic water breaks down lead in plumbing more readily, chemicals can be added to municipal water to increase the pH and thus reduce the corrosivity of the public water supply

Methods:

I. Atomic Absorption Spectrometric Method

The atomic absorption spectrometric method is subject to interference in the flame mode and requires an extraction procedure for the low concentrations common in portable waters; the electrothermal atomic absorption method doesnot require extraction.

II. Dithizone Method

The dithizone method is sensitive and is preferred by some analysts for low concentrations.

4.2.4 Atomic Absorption Spectrometric Method for determination of Arsenic and Lead

Principle

An electrically heated atomizer or graphite furnace is used. A discrete sample volume is dispensed into the graphite sample tube. Typically, determinations are made by heating the sample in three stages.

First, a low current heats the tube to dry the sample. The second, or charging stage, destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heat the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. The resultant ground-state atomic vapor absorbs monochromatic radiation from the source. A photoelectric detector measures the decreased intensity of transmitted radiation, which is a measure of concentration.

Apparatus

i. Atomic absorption spectrometer
ii. Source lamps
iii. Graphite Furnace
iv. Readout device
v. Sample dispensers
vi. Vent
vii. Cooling water supply
viii. Membrane filter apparatus

Reagents

a. Metal-free water
b. Hydrochloric acid
c. Nitric acid
d. Matrix modifiers
- Ammonium nitrate, 10%(w/v)
- Ammonium phosphate, 40%
- Calcium nitrate, 20000 mg Ca/L
- Nickel nitrate, 10000 mg Ni/L
- Phosphoric acid

e. Stock metal solutions

Calculation

i. Direct Determination:

$$\mu g \text{ metal/L} = C \times F$$

Where

C: metal concentration as read directly from the instrument or from calibration curve, µg/L

F: Dilution factor

ii. Method of additions:

$$\mu g\ metal/L = C \times F$$

Where

C: metal concentration as read from the method of addition plot, µg/L

F: Dilution factor

Figure 4.4: Atomic Absorption Spectrometer

4.2.5 Calcium

Theory

The presence of calcium in water supplies through or over deposits of limestone, dolomite, gypsum and gypsiferous shale. The calcium content may range from zero to several hundred milligrams per liter, depending on the source and treatment of the water. Small concentrations of calcium carbonate combat corrosion of metal pipes by laying down a protective coating.

Methods

I. Atomic Absorption Spectrometer Method
II. Permanganate Titrimetric Method
III. EDTA Titrimetric Method

EDTA Titrimetric method

Principle

When EDTA 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.

Reagents

i. Sodium hydroxide, NaOH, 1N
ii. Indicators
   - Murexide (ammonium purpurate) indicator
   - Erichrome Blue Black R indicator
iii. Standard EDTA titrant, 0.01 M

Procedure

2 ml of NaOH solution is added to produce a pH of 12 to 13. The solution was stirred. 0.1 to 0.2 g indicator mixture selected was added. EDTA titrant was added slowly, with continuous stirring to the proper end point. When using murexide, check end point by adding 1 to 2 drops of titrant in excess to make certain that no further color change occurs.

Calculation

$$\text{Mg Ca/L} = \text{A x B x } 400.8 \text{ / mL sample}$$

$$\text{Calcium Hardness as mg } CaCO_3\text{/L} = \text{A x B x } 1000 \text{ / mL sample}$$

A: mL titrant for sample

B: mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant at the calcium indicator end point

4.2.6 TOTAL HARDNESS

Theory

All natural waters contain dissolved cations and anions. Water dissolves many ions as it flows through minerals. Although water hardness is defined as the quantity of cations with a +2 or +3 charge, calcium ion and magnesium ion are the most common of such ions in natural water. The formation of solid calcium carbonate is an endothermic process.

Methods

I. Hardness by Titration
II. EDTA Titrimetric Method

EDTA Titrimetric Method

Principle

The quantity of "hardness ions" will be determined by titration. EDTA, a weak acid, will be used as the titrant. In its ionized form, it is able to form soluble complexes with calcium and magnesium cations. The indicator added to the sample is Eriochrome Black T. Initially, the indicator will form a complex with the cations. When complexed it is red in color. As the EDTA is added dropwise to the sample, it replaces the Erio T and forms more stable complexes with calcium and magnesium. When the indicator is released by the metal ions, it has a distinct blue color. Therefore, the endpoint of the titration is marked by the color change from red to blue.

Reagents Required

a. Standard hard water(N/50,1ml)
b. EDTA solution(N/50)
c. Ammonium chloride-ammonium hydroxide buffer (pH=10)
d. Erichrome Black T indicator solution

Procedure:

1. Pipet 25-ml of the water sample into an Erlenmeyer flask and dilute to a total volume of approximately 50 ml. Add at least one ml of pH 10 buffer solution (1/2 of a Beral pipet) to the sample. The pH should be 10. To check pH, standardize pH meter.

2. Standardize pH Meter:

a) Press mode to select pH.
b) Press setup twice and then enter to clear the existing standardization buffers.
c) Press std to access the Standardize screen. Immerse the electrode into pH buffer 7.0.
d) Press std again the initiate standardization. After the reading is stable, the meter will return to the measure screen. Remove electrode from buffer. Rinse off with DI water and blot dry with Kimwipe. Repeat steps b and c with buffer 10.0.

3. Place the pH meter electrode into the Erlenmeyer flask. Make sure the meter is in pH mode. When the meter senses that the reading has stabilized, the stable icon will appear under the reading. Record the initial pH on the data sheet.
4. Remove the pH electrode from the flask. Rinse the electrode several times over the 250mL beaker, noting the pH reading on the pH meter. When pH hovers below 8.0, dry electrode with a Kimwipe and place in pH buffer 7.0.
5. Place the magnetic stirrer in the beaker and turn on the stirrer slowly; making sure that the bar does not hit the electrode.
6. Add a few drops Eriochrome Black T indicator to the Erlenmeyer. Fill the buret with standardized EDTA. Record the initial buret reading.
7. Immediately begin to titrate the sample two drops at a time. Be careful to titrate slowly near the endpoint, as the color will take about 5 seconds to develop. Thus, add the last few drops at 3 5 second intervals. The endpoint color is blue.

Calculation

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

A: ml titration for sample

B: mg $CaCO_3$ equivalent to 1 ml EDTA titrant

4.2.7 Experimental Results of Metals Present In Water Samples

The results of the water quality tests of the presence of metals in water samples have been presented in Table 4.3. The corresponding Indian Standards (as per E.P. Rules, 1986, Schedule VI, Standards Prescribed by SPCBs) are also given in the table.

Table 4.3: Experimental Results of Metals Present in Water Samples

Sl. No.	Parameters	NALCO, Angul				RSP, Rourkela			NTPC,Talcher		Indian Standards (mg/l)
		S-1	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	
1	Iron(mg/l)	3.0	2.5	3.3	3.2	1.17	0.614	0.73	1.5	1.3	3
2	Arsenic (mg/l)	0.01	0.001	0.02	0.03	0.03	0.005	0.01	0.04	0.02	0.2
3	Lead (mg/l)	0.05	0.06	0.06	0.08	0.04	0.01	0.02	0.03	0.02	0.1
4	Calcium (mg/l)	70	76	73	78	28.44	18.96	47.4	37.92	28.44	200
5	Total Hardness (mg/l)	280	278	270	265	1516.8	1279.8	1256	284.4	758.4	1000

4.3 INORGANIC NON-METALLIC PARAMETERS

The inorganic non-metallic parameters include

1) Acidity
2) Alkalinity
3) pH
4) Chloride
5) Fluoride
6) Sulfate

4.3.1 ACIDITY

Theory

The acidity of a water sample is its capacity to neutralize hydroxide ions. Acidity may be caused by mineral acids such as sulfuric acid or hydrochloric acid or by dissolved carbon dioxide. Most commonly in drinking water, carbon dioxide is the principal cause of acidity. Acidity increases the corrosive behavior of water. Drinking water with a high acidity is likely to be corrosive to copper water pipes and to the solder which joins those pipes. High levels of copper and lead in drinking water often occur when acidic water stands in pipes for extended periods of time (such as over night). In addition to creating a possible health hazard due to dissolved metal ions, acidity in water can cause copper plumbing to develop pin hole leaks after a few years.

Principle

Acidity is generally measured by titration with sodium hydroxide to an accepted pH value. Phenolphthalein is an acid-base indicator which changes from colorless to a pink (magenta) at a pH of about 8.3. Generally, acidity is measured by titration of a water sample to pH 8.3 with NaOH titrant. Metacresol purple also changes color at pH 8.3, but gives a sharper color change than phenolphthalein. If available, its use is recommended over phenolphthalein.

Apparatus Required

a) pH meter and calibration standards.
b) Magnetic stirrer and stirring bar.
c) Volumetric flask: 1000-mL and 100-mL.
d) Buret: 50-mL, glass.
e) Polyethylene bottle: 1-L.

Reagents Required

a. Carbon dioxide-free water
b. Potassium hydrogen phthalate (KHP), 0.05 N
c. Standard sodium hydroxide titrant, 0.025 N
d. Phenolphthalein indicator solution, 0.5%
e. Metacresol purple indicator solution, 0.1%

Procedure

1. Begin by obtaining one or more water samples as suggested or provided by the instructor
2. Measure and record the pH of the water with a calibrated pH meter.
3. Following cleaning of a 50-mL buret, rinse it with purified water followed by several rinses with 0.025 N NaOH.
4. Fill the buret with the NaOH solution, make sure there are no air bubbles in the tip, and make sure the meniscus is readable at close to 0.00 mL on the buret scale.

5. Measure 100.0 mL of the water sample to be analyzed into a 250-mL erlenmeyer flask with as little splashing or turbulence as possible.
6. A pipet is preferred but graduated cylinder may be used if no pipet is available.
7. Titrate to a phenolphthalein or metacresol-purple endpoint. If the water is highly acidic, smaller volumes of the sample may be titrated as seems appropriate.
8. Do at least duplicate (preferably triplicate) titrations on each sample being investigated.
9. If the alkaline color of the indicator is observed before any titrant is added, report zero acidity and go on to measurement of alkalinity.

Calculations

Acidity is expressed in terms of milligrams of calcium carbonate per liter.

Acidity = (ml NaOH titrant) x (normality of NaOH) x (50,000) / (ml of water sample)

4.3.2 ALKALINITY

Theory

Alkalinity is the measure of a water sample's ability to neutralize hydrogen ions (its acid-neutralizing ability). Alkalinity may be caused by dissolved strong bases such as sodium hydroxide or potassium hydroxide (and other hydroxide-containing compounds), and it may also be caused by dissolved carbonates, bicarbonates, borates, and phosphates. The measured alkalinity is the total of all of these species found in a water sample. For the sake of simplicity, it is expressed in terms of mg $CaCO3$/L although many species other than dissolved calcium carbonate may actually contribute to the alkalinity.

Apparatus Required

a. Magnetic stirrer and stirring bar.
b. Volumetric flask: 1000-mL and 100-mL.
c. Buret: 50-mL, glass.

Reagents

a) Sodium carbonate solution ($Na2CO3$), 0.05 N
b) Standard hydrochloric acid titrant, 0.02 N
c) Bromcresol green indicator solution, 0.1%

Procedure

1. Rinse the 50-mL buret with several rinses with 0.02 N HCl.
2. Fill the buret with the HCl solution, make sure there are no air bubbles in the tip, and make sure the meniscus is readable at close to 0.00 mL on the buret scale.
3. Measure 100.0 mL of the water sample to be analyzed into a 250-mL erlenmeyer flask.
4. Titrate to a bromcresol green (pH = 4.5) endpoint.
5. If the water is high in alkalinity, smaller volumes of the sample may be titrated as seems appropriate.
6. Do at least duplicate (preferably triplicate) titrations on each sample being investigated.

Calculations

Alkalinity is expressed in terms of milligrams of calcium carbonate per liter.

$$\text{Alkalinity} = (\text{ml HCl titrant}) \times (\text{normality of HCl}) \times (50{,}000) / (\text{ml of water sample})$$

4.3.3 pH

Theory

Measurement of pH is one of the most important and frequently used tests in water chemistry. Practicably every phase of water supply and waste water treatment, e.g., acid-base neutralization, water softening, precipitation, coagulation, disinfection and corrosion control, is pH dependent.

pH is a measure of the hydrogen ion concentration of the water as ranked on a scale of 1.0 to 14.0. The lower the pH of water, the more acidic it is. The higher the pH of water, the more basic, or alkaline, it is. pH affects many chemical and biological processes in water and different organisms have different ranges of pH within which they flourish.

Principle

The basic principle of pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. The electromotive force produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

Apparatus

i. pH meter
ii. Voltmeter with high input impedance
iii. Reference electrode
iv. Glass electrode
v. Stirrer
vi. Flow chamber

pH meter

A pH meter measures essentially the electro-chemical potential between a known liquid inside the glass electrode (membrane) and an unknown liquid outside. Because the thin glass bulb allows mainly the agile and small hydrogen ions to interact with the glass, the glass electrode measures the electro-chemical potential of hydrogen ions or the potential of hydrogen.

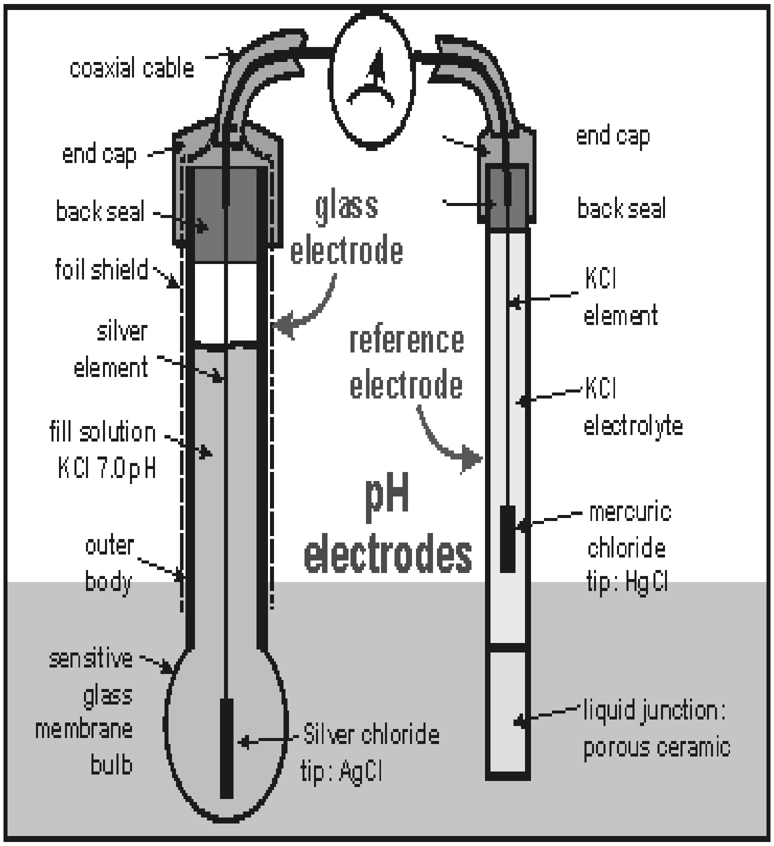

Figure 4.5: Schematic Diagram of pH Electrodes

To complete the electrical circuit, also a reference electrode is needed. Note that the instrument does not measure a current but only an electrical voltage, yet a small leakage of ions from the reference electrode is needed, forming a conducting bridge to the glass electrode. A pH meter must thus not be used in moving liquids of low conductivity (thus measuring inside small containers is preferable).

The calomel reference electrode consists of a glass tube with a potassium chloride (KCl) electrolyte which is in intimate contact with a mercuric chloride element at the end of a KCL element. It is a fragile construction, joined by a liquid junction tip made of porous ceramic or similar material. This kind of electrode is not easily 'poisoned' by heavy metals and sodium. The glass electrode consists of a sturdy glass tube with a thin glass bulb welded to it. Inside is a known solution of potassium chloride (KCl) buffered at a pH of 7.0. A silver electrode with a silver chloride tip makes contact with the inside solution.

To minimise electronic interference, the probe is shielded by a foil shield, often found inside the glass electrode. Most modern pH meters also have a thermistor temperature probe which allows for automatic temperature correction, since pH varies somewhat with temperature. In this method, a PE 138 water quality analyser of Elico make (Figure 4.6) was used.

Procedure

i. Stir the water sample vigorously using a clean glass stirring rod.
ii. Pour a 40 inL ± 5 mL sample into the glass beaker using the watch glass for a cover.
iii. Let the sample stand for a minimum of one hour to allow the temperature to stabilize; stirring it occasionally while awaiting. Measure the temperature of the sample and adjust the temperature controller of the pH meter to that of the sample temperature. This adjustment should be done just prior to testing. On meters, with an automatic temperature control, follow the manufacturer's instructions.
iv. Standardize the pH meter by means of the standard solutions provided. Temperature and adjustments must be performed.
v. Immerse the electrode(s) of the pH meter into the water sample and turn the beaker slightly to obtain good contact between the water and the electrode(s).

Figure 4.6: PE 138 Water Quality Analyzer

vi. The electrode(s) require immersion 30 seconds or longer in the sample before reading to allow the meter to stabilize. If the meter has an auto read system, it will automatically signal when stabilized.

vii. Read and record the pH value to the nearest tenth of a whole number. If the pH meter reads to the hundredth place, a round of rule will apply as follows: If the hundredth place digit is less than 5, leave the tenth place digit as is. If it is greater than 5, round the tenth place digit up one unit. If the hundredth place digit equals 5, round the tenth place digit to the nearest even number.

viii. Rinse the electrode(s) well with distilled water, then dab lightly with tissues to remove any film formed on the electrode(s). Caution: Do not wipe the electrodes, as this may result in polarization of the electrode and consequent slow response.

4.3.4 Chloride

Theory

Chloride, in the form of chloride ion, is one of the major inorganic anions in water and waste-water. The concentration of chloride in water is variable and dependent on the chemical composition of water. High chloride content may harm metallic pipes and structures, as well as growing plants.

Methods

I. Argentometric Method

This method is suitable for use in relatively clear waters when 0.15 to 10 mg chloride ion are present in the portion titrated.

II. Mercuric Nitrate Method

The end point of this method is easier to detect.

III. Potentiometric Method

This method is suitable for colored or turbid samples. The potentiometric method can be used without a pretreatment step for samples containing ferric ions, chromic, phosphate, and ferrous and other heavy metal ions.

IV. Automated Ferricyanide Method

This method is an automated technique.

Argentometric Method

Principle

This test measures the soluble chloride Ion concentration in the mud filtrate. The Chloride can come from sodium chloride, calcium chloride or potassium chloride. Also, for the titration to work correctly the pH of the filtrate needs to be only weakly basic (pH = 8.3). This is the reason for the first step in the procedure. There are two chemical reactions taking place simultaneously during the titration.

$$Ag^{+} + Cl^{-} \rightarrow AgCL$$

$$2\ Ag\ (+) + CrO_4 \rightarrow Ag_2\ CrO_4$$

The first reaction, the formation of silver chloride, accounts for the appearance of the white specs or milky appearance during the titration. The formation of the silver chromate, which is red, will not start until all the chloride Ions are tied up as silver chloride. The silver nitrate will then react with the chromate from the potassium chromate indicator to form silver chromate. So, for the above two reactions to occur, the filtrate needs to be weakly basic (pH = 8.3). High pH will precipitate silver oxide.

Apparatus

a. Erlenmeyer flask, 250ml
b. Buret, 50 ml

Reagents

i. Potassium Chromate Indicator
ii. Standard Silver Nitrate Titrant
iii. Sodium Hydroxide
iv. Phenolphthalein Indicator
v. Hydrogen Peroxide
vi. Sulfuric Acid

Procedure

a) Pipette 1.0 ml of filtrate or sample to be tested into titration dish.

b) Add 2 – 3 drops of phenolphthalein indicator to the filtrate.
c) If a pink color appears, titrate with N/50 sulfuric acid until the color changes from pink to that of the original sample. If no pink color appears, the test can be continued.
d) If needed, add 25 – 50 mls of distilled water. This serves to dilute the dark color of a deeply colored filtrate. It does not influence the test in any way if there are no chlorides present in the distilled water. If any water other than distilled water is used, the chloride in it must be accounted for by titration before adding the filtrate to it.
e) Add 10 to 15 drops of potassium chromate indicator to give filtrate a bright yellow color.
f) Add silver nitrate from a pipette drop wise, stirring continuously with a stirring rod, until the sample just turns from yellow to an orange-red.

Calculation

$$\text{Chloride (mg/l)} = (A - B) \times N \times 35450/\text{ ml sample}$$

A: ml titration for sample
B: ml titration for blank
N: Normality of $AgNO_3$

4.3.5 Fluoride

Theory

A fluoride concentration of approx. 1mg/l in drinking water effectively reduces dental caries without harmful effects on health. Accurate determination of fluoride has increased in importance with the growth of the practice of fluoridation of water supplies as a public health measure. Maintenance of an optimal fluoride concentration is essential in maintaining effectiveness and safety of the fluoridation procedure.

Methods

I. Preliminary Distillation Method

Fluoride can be separated from other nonvolatile constituents in water by conversion to hydrofluoric or fluosilicic acid and subsequent distillation. The conversion is accomplished by using a strong, high boiling acid.

II. Electrode Method

This method is suitable for fluoride concentrations from 0.1 to more than 10 mg/l. Adding the prescribed buffer frees the electrode method from most interferences that adversely affect the colorimetric methods and necessitate preliminary distillation.

III. SPADNS Method

Color determinations are made photometrically, using either a filter photometer or a spectrometer. A curve developed from standards can be used for determining the fluoride concentration of a sample or the concentration of a sample can be calculated on the basis of a pair of standards.

IV. Alizarin Visual Method

This method is suitable only for fluoride concentrations in the range of 0.05 to 1.4 mg/l, and sensitivity is limited by the color matching of the glass ware. This method is subject to interference from substances commonly in water.

Electrode Method

Principle

The fluoride electrode is a selective ion sensor. The key element in the fluoride electrode is the laser-type doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations. The crystal contacts the sample solution at one face and an internal reference solution at the other. The fluoride electrode can be used with a standard calomel reference electrode and any modern pH meter. The fluoride measures the ion activity of fluoride in solution rather than concentration. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species.

Apparatus

a) Expanded-scale or digital pH meter
b) Sleeve-type reference electrode
c) Fluoride electrode
d) Magnetic stirrer
e) Timer

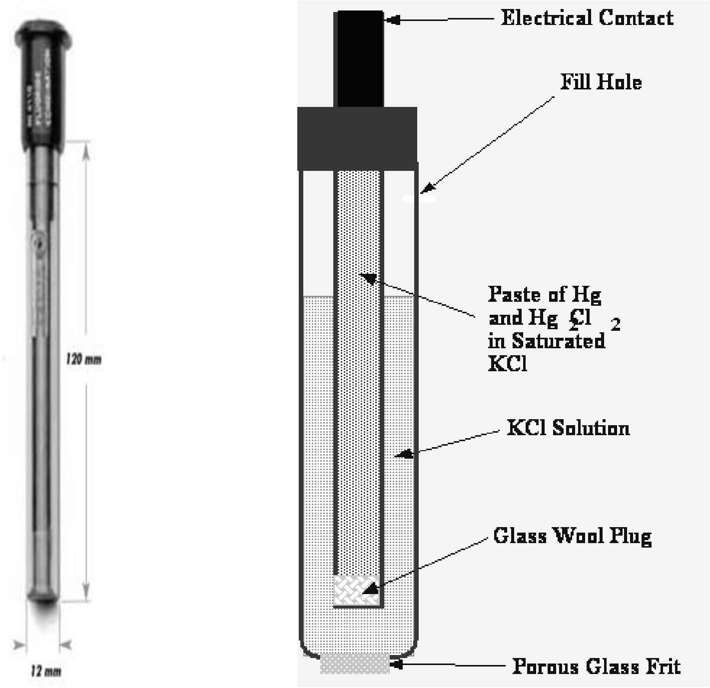

Figure4.7: Fluoride Electrode and Calomel Electrode

Reagents

i. Stock fluoride solution
ii. Standard fluoride solution
iii. Fluoride buffer

Procedure

The electrodes were immersed in the 0.5 mg F^-/L standard and the developed potential was measured while stirring on a magnetic stirrer. The electrodes were allowed to remain in solution for 3 min before taking a final mill volt reading. A layer of insulating material stirrer and beaker minimizes solution heating. The electrodes were withdrawn, rinsed with distilled water and blot dried between readings. The measurements were repeated with increasing fluoride concentrations, then with sample.

Calculation

$$\text{Fluoride (mg/l)} = \mu g\ F^- / \text{ ml sample}$$

4.3.6 Ammonia

Theory

Ammonia is present naturally in surface and wastewaters. Its concentration generally is low in ground waters because it adsorbs to soil particles and clays and is not leached readily from solids. It is produced largely by deamination of organic nitrogen-containing compounds and by hydrolysis of urea. At some water treatment plants ammonia is added to react with chlorine to form combined chlorine residual.

Method

I. Preliminary Distillation Step
II. Nesslerization Method(Direct and Following Distillation)
III. Phenate Method
IV. Titrimetric Method
V. Ammonia-Selective Electrode Method

Titrimetric Method

Principle

The titrimetric method is used only on samples that have been carried through preliminary distillation. This method is used especially for ammonia concentration up to 5 mg/L. Distillation with sulfuric acid is mandatory when interferences are present.

Apparatus

a. Distillation Apparatus
b. pH meter

Reagents

a. Mixed indicator solution
b. Indicating boric acid solution
c. Standard sulfuric acid titrant,0.02 N

Procedure

The ammonia was titrated in distillate with standard 0.02 N H_2SO_4 titrant until indicator turned a pale lavender.

The following table is useful in selecting volume for the distillation and titration method.

Ammonia Nitrogen in Sample (mg/L)	Sample Volume (mL)
5-10	250
10-20	100
20-50	50
50-100	25

Calculation

i. Liquid samples:

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

ii. Sludge or sediment samples:

$$\text{mg } NH_3^{-}N / kg = (A-B) \times 280 / \text{g dry weight sample}$$

A: Volume of H_2SO_4 titrated for sample, ml

B: Volume of H_2SO_4 titrated for blank, ml

4.3.7 Sulfate

Theory

Sulfate is widely distributed in nature and may be present in nature and may be present in natural waters in concentrations ranging from a few to several thousand milligrams per liter.
Mine drainage wastes may contribute large amounts of SO_4^{2-} through pyrite oxidation. Sodium and Magnesium sulfate exert a cathartic action.

Methods

I. Gravimetric Method with Ignition of Residue
II. Gravimetric Method with Drying of Residue
III. Turbidimetric Method
IV. Automated Methylthymol Blue Method

Method I and II are suitable for sulfate concentrations above 10 mg/l. Method III is applicable in the range of 1 to 40 mg/L. Method IV is the procedure of choice when the equipment is available; about 30 samples can be analyzed per hour.

Gravimetric Method with Ignition of Residue

Principle

Sulfate is precipitated in a hydrochloric acid (HCl) solution as barium sulfate ($BaSO_4$) by the addition of barium chloride ($BaCl_2$). The precipitation is carried out near the boiling temperature, and after a period of digestion the precipitate is filtered, washed with water until free of chloride ion, ignited or dried, and weighed as ($BaSO_4$).

Interferences

The gravimetric determination of sulfate is subject to many errors, both positive and negative. Interferences leading to high results-suspended matter, silica, nitrite and occluded mother liquor in the precipitate are the principal factors in positive errors. Interferences leading to low results-alkali metal sulfates frequently yield low results.

Apparatus

i. Steam bath
ii. Drying oven
iii. Muffle furnace
iv. Desiccator
v. Analytical Balance
vi. Filter
vii. Filtering apparatus

Reagents

a) Methyl red indicator solution
b) Hydrochloric acid
c) Barium chloride solution
d) Silver nitrate-nitric acid
e) Silicone fluid

Procedure

The method of choice for sulfate in waters and wastewaters is the precipitative gravimetric procedure using barium. If Ba(+II) is added in excess under acidic conditions, $BaSO_4$ is precipitated quantitatively. The reaction is allowed to continue for 2 hours or more at 80-90^oC. This is to encourage the formation of $BaSO_4$ crystals (non-filterable) from the initially formed colloidal precipitate (partially filterable). The precipitate is washed, and then dried at 800^0C for 1 hour. Low pH is needed to avoid the precipitation of $BaCO_3$ and $Ba_3(PO_4)_2$. Positive bias may result from acid-resistant insoluble matter such as silica, sulfites which may oxidize to sulfate, and nitrate and chloride which will associate with barium and co-precipitate to a small extent with the barium sulfate. Negative bias may result from the presence of certain heavy metals (e.g., Cr, Fe) which can form soluble complexes with sulfate.

Calculation

$$\text{mg } SO_4^{2-}/L = \text{mg } BaSO_4 \times 411.6/\text{mL sample}$$

4.3.8 Experimental Results of Inorganic Nonmetallic Constituents in Water Samples

The results of the water quality tests of inorganic nonmetallic constituents in water samples have been presented in Table 4.4. The corresponding Indian Standards (as per E.P. Rules, 1986, Schedule VI, Standards Prescribed by SPCBs) are also given in the table.

Table 4.4: Experimental Results of Inorganic Nonmetallic Constituents in Water Samples

Sl. No.	Parameters	NALCO, Angul				RSP, Rourkela			NTPC,Talcher		Indian Standards (mg/l)
		S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	
1	Alkalinity (mg/l)	200	230	199	240	102	306	101.2	132	76.5	600
2	pH	8.9	8.7	8.6	8.0	6.9	7.2	7.0	5.8	8.2	5.5-9.0
3	Chloride (mg/l)	121	131	129	126	121.4	60.72	101.2	105	40.48	1000
4	Fluoride (mg/l)	1.5	1.7	1.89	2.1	3	0.5	1.5	1.5	1	2
5	Ammonia (mg/l)	1	1.2	1.1	1.3	0.61	1.22	4.8	2	0.5	5
6	Sulfate (mg/l)	32	34	36	31	160	35	38	50	40	200

4.4 ORGANIC PARAMETERS

The organic parameters include

1) Biological Oxygen Demand
2) Chemical Oxygen Demand
3) Total Organic carbon
4) Dissolved Oxygen

4.4.1 Biological Oxygen Demand

Theory

The BOD is a chemical procedure for determining the uptake rate of dissolved oxygen by the biological organisms in a body of water.

The test measures the oxygen required for the biochemical degradation of organic material and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron.

It also measures the oxygen used to oxidize reduced forms of nitrogen unless their oxidation is prevented by an inhibitor.

Methods

I. Dilution Method
II. Manometric Method

Dilution Method

Principle

The method consists of placing a sample in a full, air tight bottle and incubating the bottle under specific conditions for a specific time. Dissolved oxygen (DO) is measured initially and after incubation. The BOD is computed from the difference between initial and final DO.

Apparatus

i. Incubation Bottles (250-300 ml)
ii. Air Incubator (20 ± 1°C)
iii. DO meter
iv. Burette

Figure 4.8: BOD incubator

Reagents

a) Phosphate buffer
b) Mohr's salt
c) Magnesium sulfate solution
d) Calcium chloride solution
e) Ferric Chloride solution
f) Acid and alkali solution
g) Sodium sulfate solution
h) Nitrification inhibitor

Dilution Technique

1. The B.O.D. of the sample was estimated and suitable dilutions was selected from the following table: 4.5

Estimated BOD_5 (mg/L)	**Suggested Sample Volumes (mL)**	**Estimated BOD_5 (mg/L)**	**Suggested Sample Volumes (mL)**
< 5	200, 250, 300	90 - 150	5, 10, 15
< 10	100, 150, 200	150 - 300	3, 5, 10
10 - 30	25, 50, 100	300 - 700	1, 3, 5
30 - 60	15, 25, 50	700 - 1500	0.5, 1, 3
60 - 90	10, 15, 25	1500 - 2500	0.25, 0.5, 1

Standard Methods provides additional guidance as follows: use less than 3 mL for strong industrial wastes, 3-15 mL for raw and settled wastewater, and 15-75 mL for biologically treated effluent

2. Using a large-tipped, volumetric pipette - for samples less than 50 ml - or a graduated cylinder for larger sample volumes, the proper amount of well-mixed sample was measured into thoroughly cleaned and rinsed 300 ml bottles. Dilutions under 3 mL was made by diluting the waste in a graduated cylinder before pipetting.

3. Dilution water was prepared immediately before use, or, *except for the addition of the phosphate buffer*, days or weeks ahead of time. 1 ml or each nutrient solution per liter of dilution water was added.
4. The phosphate buffer is the critical nutrient in stimulating contaminating growths so it was added the day the water was used.
5. Distilled water was allowed to equilibrate in the incubator or with outside air for at least 24 hours at 20°C before use.
6. To avoid dust or dirt contamination while allowing oxygenation, a paper towel, cotton plug, or sponge was used to cover the bottle opening.
7. Each BOD bottle was filled by slowly adding sufficient dilution water so that the stopper can be inserted without leaving an air bubble but not so much that there is overflow. The siphon hose was made of surgical gum (latex rubber), polypropylene or polyethylene to avoid introducing BOD into the dilution water.
8. When volumes of sample used exceed 150 ml, additional nutrients was added to sample bottle.
9. An additional 0.1 mL of nutrients was added for each 50 mL of sample used in excess of 150 mL. For example, if sample size is 200 ml, an additional 0.2 ml is required.
10. The two bottles was completely filled with dilution water to be incubated as blanks.

Incubation and Dissolved Oxygen (DO) Determinations

1. DO meter was calibrated each day of use and check membrane on probe. The barometric pressure was recorded after each day of analysis. This can be obtained from a barometer in the laboratory. Alternatively, barometric pressure readings can be obtained via the Internet, from a local radio or television news station, or from a local airport. Barometric pressure readings should not be corrected to sea level.
2. The DO of the two dilution water blanks and all sample bottles was determined and was recorded on data sheet as Initial DO.
3. The samples and the dilution water blanks were placed in a 20 ± 1°C incubator for 5 days. Water seals with dilution water were filled and cap to reduce evaporation from seals. Check daily; water was added to seals if necessary. *Due to the 5 day testing*

period, certain samples require that set-ups and run-outs of results be performed by different individuals.

4. Before removing the caps, the water above the cap was pour off.
5. After 5 days the DO was determined of the two dilution water blanks and the sample bottles.

Calculation

When dilution water is not seeded:

$$\mathbf{BOD,\ mg/l = (D_1-D_2) / P}$$

When dilution water is seeded:

$$\mathbf{BOD,\ mg/l = (D_1-D_2) - (B_1-B_2)\ f / P}$$

where

D_1: DO of diluted sample immediately after preparation
D_2: DO of diluted sample after 5 days incubation
P: Decimal volumetric fraction of sample used
B_1: DO of seed control before incubation
B_2: DO of seed control after incubation

4.4.2 Chemical Oxygen Demand

Theory

The amount of oxygen needed to consume the organic and inorganic materials is called Chemical Oxygen Demand (COD). The COD is used as a measure of the oxygen equivalent of the organic equivalent of the organic matter content of a sample. Potassium dichromate is considered the best oxidant due to its strong oxidizing ability, its applicability to a wide variety of samples and ease of manipulation makes it very efficient.

Methods

I. Open Reflux Method
II. Closed Reflux, Titrimetric Method
III. Closed Reflux, Colorimetric Method

Closed Reflux Titrimetric Method

Principle

A sample is refluxed in strongly acid solution with a known excess of potassium dichromate. After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent.

Apparatus

i. Erlenmeyer flask
ii. Small beaker
iii. Titration apparatus:
    - 25 or 50 mL burette, graduated in 0.1 mL
    - burette support
    - 100 mL graduated cylinder
    - rubber-tipped stirring rod, or magnetic stirrer and stir bar
    - white porcelain evaporating dish, 4.5 inches in diameter

iv. Reflux apparatus:
    - 500 or 250 mL erlenmeyer flasks with ground-glass 24/40 neck
    - 300-mm jacket Liebig, West, or equivalent condenser with 24/40 ground-glass joint
    - hot plate with sufficient power to produce at least 1.4 W/cm^2 of heating surface

v. Blender
vi. Pipets
vii. Glass beads
viii. Fume hood

Reagents

a) Potassium dichromate
b) Mohr’s salt

c) Mercuric sulfate
d) Sulfuric acid
e) Ferroin indicator solution

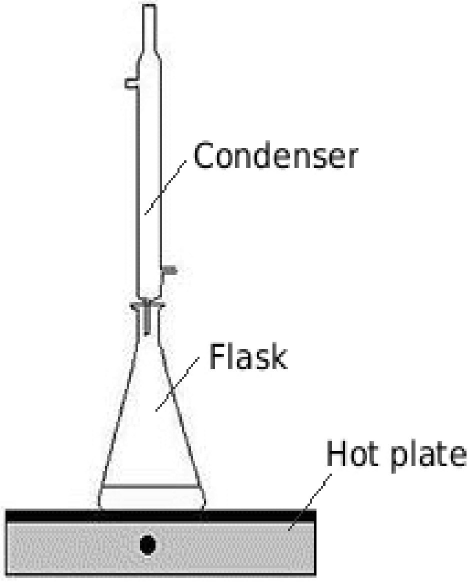

Figure 4.9: Reflux Apparatus

Procedure

1) Standardize the ferrous ammonium sulfate.

a) Place 10.0 mL of 0.250 N potassium dichromate solutions in a 500 mL erlenmeyer flask.
b) Dilute the potassium dichromate solution to 100 mL with distilled water.
c) Add 30 mL of concentrated sulfuric acid. Add the acid slowly while mixing the solution.
d) Cool the solution to room temperature.
e) Add 2 or 3 drops of ferroin indicator.
f) Titrate with ferrous ammonium sulfate until the solution changes from a blue-green color to a reddish-brown color. Record the amount of titrant used in the Data section.
g) Calculate the normality of the ferrous ammonium sulfate using the following formula.

2) Prepare the sample water.

a) If the sample is not homogeneous, mix it in a blender.
b) Pipet a suitable amount of the sample into a 500 mL refluxing flask.

c) Add 1 gram of mercuric sulfate to the sample.

d) Add several glass beads to the solution.

e) Very slowly, add 5.0 mL of sulfuric acid reagent. Swirl the flask while adding the reagent to help dissolve the mercuric sulfate.

f) Add 25.0 mL of the 0.250 N potassium dichromate solution and mix.

3) Prepare a blank.

a) Pipet a volume of distilled water equal to that of the sample into a 500 mL refluxing flask.

b) Add 1 gram of mercuric sulfate to the distilled water.

c) Add several glass beads to the solution.

d) Very slowly, add 5.0 mL of sulfuric acid reagent. Swirl the flask while adding the reagent to help dissolve the mercuric sulfate.

e) Add 25.0 mL of the 0.250 N potassium dichromate solution and mix.

4) Reflux both the sample flask and the blank flask.

a) Attach the sample flask and the blank flask to separate condensers and turn on the cooling water.

b) Add 70 mL of sulfuric acid reagent to each flask through the open end of the condenser. Swirl the flask several times while adding the sulfuric acid reagent.

Figure 4.10: Operational Procedure of COD

c) Cover the end of the condenser with a small beaker to prevent foreign material from entering the reflux mixture.

d) Turn on the hot plate and reflux (boil) the mixture for two hours.

e) Cool the flask and condenser.

f) Wash down the inside of the condenser with distilled water and then remove the condenser.

5) Titrate both the sample flask and the blank flask.

a) Dilute the contents of each flask to approximately twice its volume with distilled water.

b) Add 2 or 3 drops of ferroin indicator to each flask.

c) Titrate each flask with ferrous ammonium sulfate until the contents change color from blue-green to reddish-brown and the color change remains for 1 minute or longer. Record the amount of titrant used in the Data section.

6) Calculate the COD of the sample using the following formula:

$$\text{COD, mg/L} = (A-B) \times M \times 8000 / \text{Volume of Sample in ml}$$

Where:

A: mL of titrant used for sample

B: mL of titrant used for blank

M: normality of ferrous ammonium sulfate

4.4.3 Experimental Results of Organic Parameters in Water Samples

The results of the water quality tests of the organic parameters in water samples have been presented in Table 4.6. The corresponding Indian Standards (as per E.P. Rules, 1986, Schedule VI, Standards Prescribed by SPCBs) are also given in the table.

Table: 4.6 Experimental Results of Organic Parameters in Water Samples

Sl. No.	**Parameters**	**NALCO, Angul**				**RSP, Rourkela**			**NTPC,Talcher**		**Indian Standards (mg/l)**
		S-1	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	
1	BOD (mg/l)	25	26	29	27	16	10	12	14	13	30
2	COD (mg/l)	96	74	68	56	76	64	69	62	58	250

CHAPTER

5

DISCUSSION AND CONCLUSION

5. DISCUSSION AND CONCLUSIONS

5.1 Discussions

The turbidity and color of different water samples are shown in Figure 5.1.

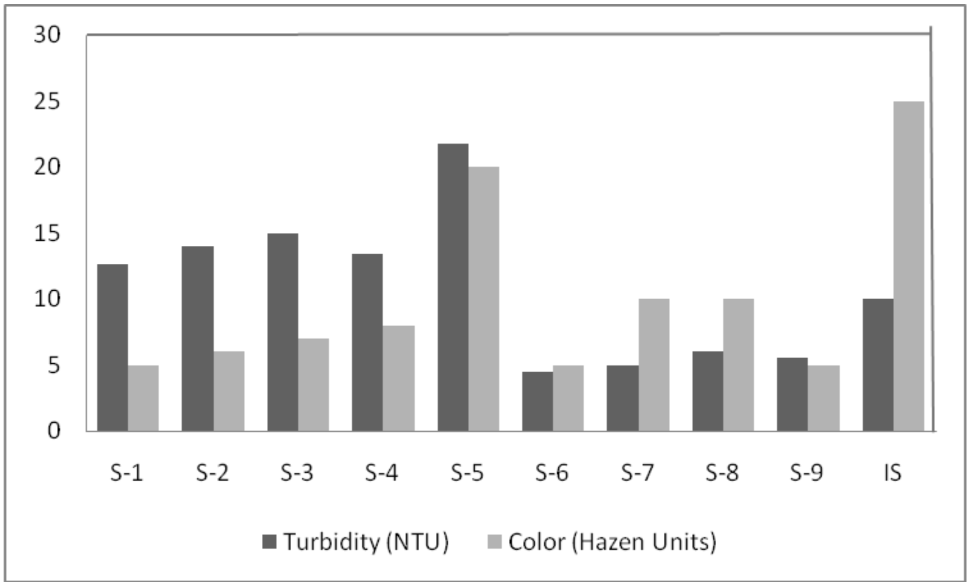

Figure 5.1: Color and Turbidity of different water samples

It may be observed from table 4.2 and figure 5.1 that the turbidity ranged from 4.5 to 21.7 NTU in the study area. The water sample S-5 had a very high turbidity in comparison to other samples. The turbidity of S-5 was found to be 21.7 NTU which exceeds the permissible limit. The water samples S-3, S-2, S-4 and S-1 also had turbidity beyond the permissible limit. The turbidity of water samples S-6, S-7, S-8 and S-9 was within the limit. The prescribed limit of turbidity is 10 NTU (as per E.P. Rules, 1986, Schedule VI, Standards Prescribed by SPCBs).

The color varied from 5 Hz to 20 Hz in the study area. The color of all water samples was within the permissible limit. The prescribed limit of color is 25 Hazen Units (Hz).

The conductivity, total dissolved solids (TDS) and total suspended solids (TSS) of different water samples are shown in Figure 5.2.

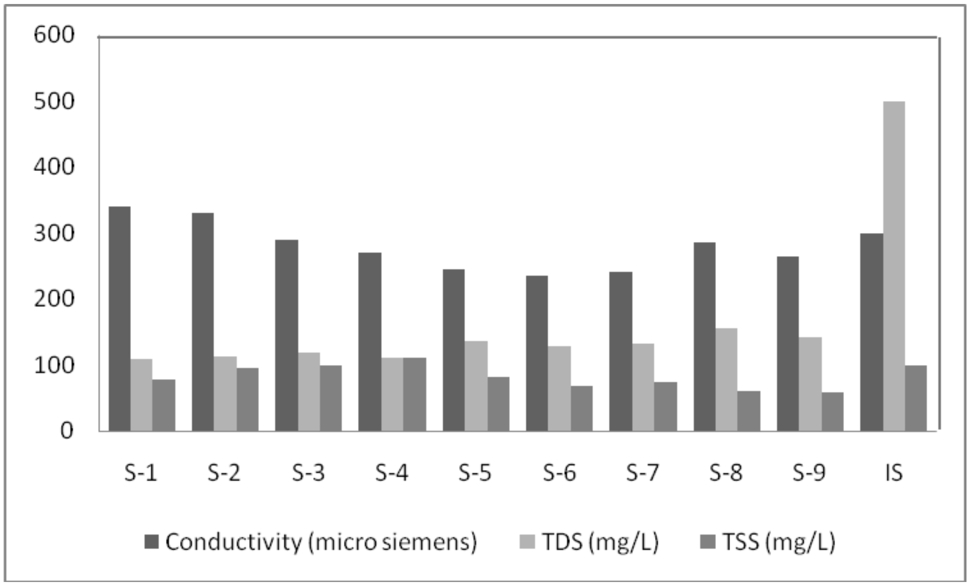

Figure 5.2: Conductivity, TDS and TSS of different water samples

It may be observed from Table 4.2 and figure 5.2 that the conductivity ranged from 234 to 340 micro siemens in the study area. The water sample S-1 and S-2 had high conductivity in comparison to other samples and the values exceeded the permissible limit. The conductivity of all other water samples was within the limits. The prescribed limit of conductivity is 300 micro-siemens.

The Total Dissolved Solids ranged from 108 to 155 mg/l in the study area. The water sample S-8 had a high TDS in comparison to other samples. However the value was within the permissible limit. The TDS of all water samples was within the limits. The prescribed limit of TDS is 500 mg/l.

The Total Suspended Solids ranged from 58 to 111 mg/l in the study area. The water sample S-4 had a high TSS in comparison to other samples. The TSS of S-4 was found to be 111 mg/l which exceeds the permissible limit. The TSS of all other water samples was within the limits. The prescribed limit of TSS is 100 mg/l.

The arsenic, iron and lead content of different water samples are shown in Figure 5.3. It may be observed from Table 4.3 and figure 5.3 that the arsenic content ranged from 0.001 to 0.04 mg/l in the study area. The arsenic content of all water samples was within the limits. The prescribed limit of arsenic is 0.2 mg/l.

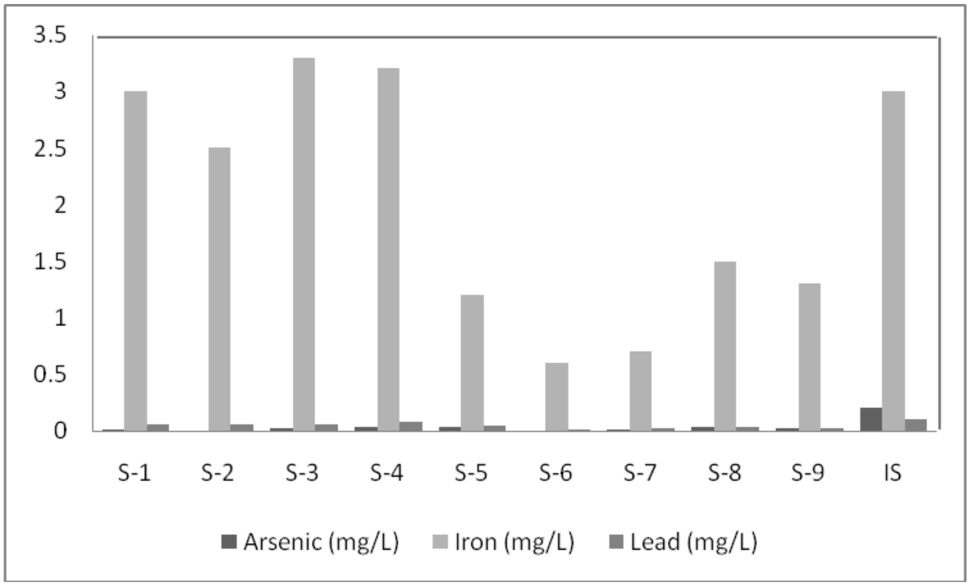

Figure 5.3: Arsenic, Iron and Lead of different water samples

The iron content varied from 0.614 to 3.3 mg/l in the study area. The iron content of S-3 and S-4 was higher than the other water samples and the values were higher than the permissible limit. The iron content of all other water samples was within the limit. The prescribed limit of iron is 3 mg/l.

The lead content varied from 0.01 to 0.08 mg/l in the study area. The lead content of S-4 was comparatively higher than the other water samples. The lead content of all water samples was within the permissible limit. The prescribed limit of lead is 0.1 mg/l.

The calcium and total hardness of different water samples are shown in figure 5.4.

It may be observed from table 4.3 and figure 5.4 that the calcium content varied from 19 to 78 mg/l in the study area. The calcium content of all water samples was within the permissible limit. The prescribed limit of lead is 0.1 mg/l.

The Total Hardness ranged from 265 to 1517 mg/l in the study area. The total hardness of S-5, S-6 and S-7 was much higher than the permissible limit. The hardness of S-5 was found to be 1517 mg/l and the value was highest among all water samples. It was then followed by S-6 and S-7. The total hardness of S-1, S-2, S-3, S-4, S-8 and S-9 was within the limit. The prescribed limit of total hardness is 1000 mg/l.

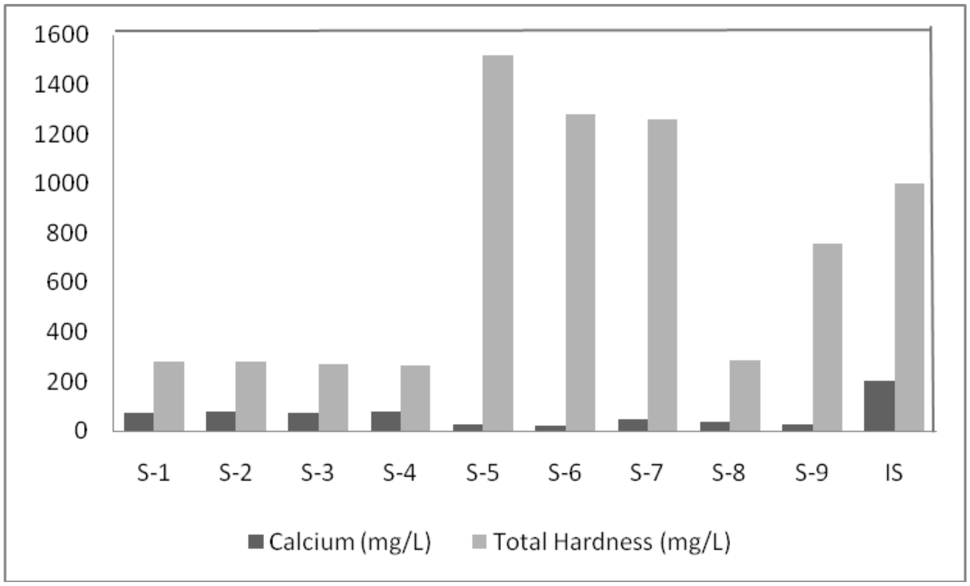

Figure 5.4: Calcium and Total Hardness of different water samples

The ammonia, fluoride and pH of different water samples are shown in figure 5.5.

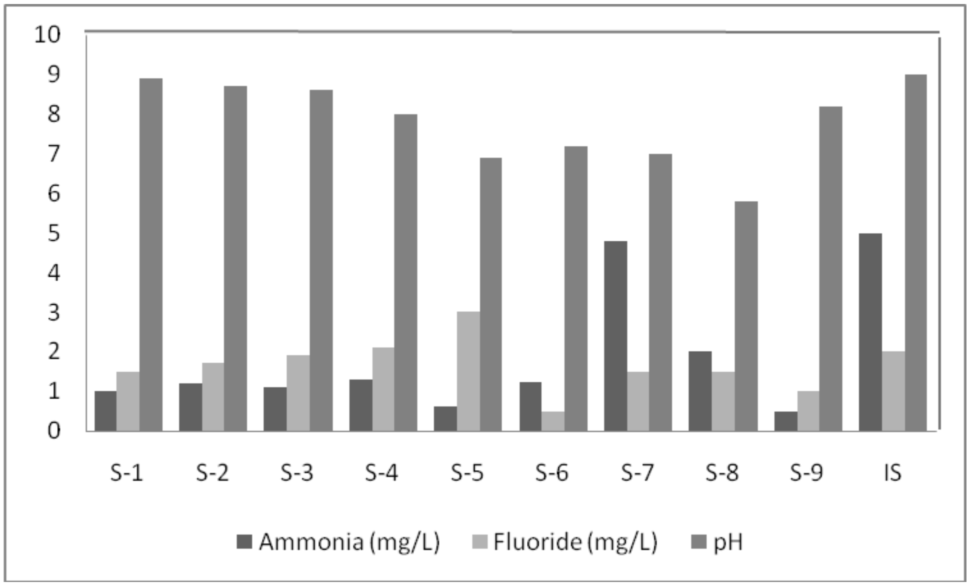

Figure 5.5: Ammonia, Fluoride and pH of different water samples

It may be observed from table 4.4 and figure 5.5 that the ammonia ranged from 0.5 to 4.8 mg/l in the study area. The ammonia of S-7 was comparatively higher than the other water samples. However, the value was within the permissible limit. The ammonia content of all water samples was within the limit. The prescribed limit of ammonia is 5 mg/l.

The fluoride content in the water samples ranged from 0.5 to 3 mg/l in the study area. The water sample S-5 had a very high fluoride content which exceeds the permissible limit. The fluoride content of all other samples except S-5 and S-4 was within the limit. The prescribed limit of fluoride is 2 mg/l.

The pH in the water samples ranged from 5.8 to 8.2 in the study area. The water sample S-8 had a quite low pH in comparison with other samples. The pH of S-9 was highest among all water samples. The pH of all samples was within the permissible limit. The prescribed limit of pH is 5.5 – 9.0 (as per E.P. Rules, 1986, Schedule VI, Standards Prescribed by SPCBs).

The alkalinity, chloride and sulfate of different water samples are shown in figure 5.6.

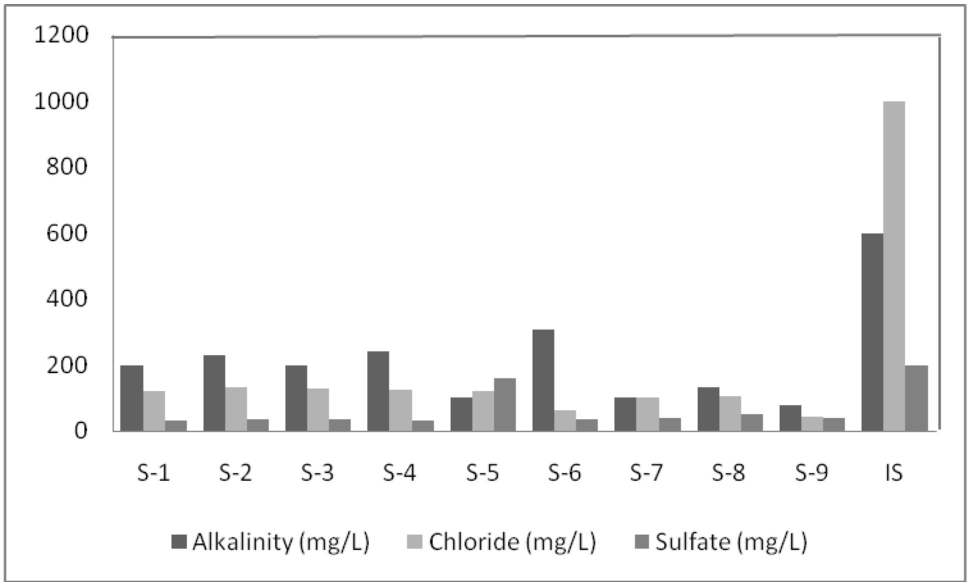

Figure 5.6: Alkalinity, Chloride and Sulfate of different water samples

It may be observed from table 4.4 and figure 5.6 that the alkalinity ranged from 76.5 to 306 mg/l in the study area. The alkalinity of S-6 was comparatively higher than the other water samples. However, the value was within the permissible limit. The alkalinity of all water samples was within the limit. The prescribed limit of alkalinity is 600 mg/l.

The chloride varied from 60 to 131 mg/l in the study area. The chloride content of all water samples was within the permissible limit. The chloride content of S-9 was lowest among all the water samples. The prescribed limit of chloride is 1000 mg/l.

The sulfate content of the water samples ranged from 31 to 160 mg/l in the study area. The sulfate content of S-5 was comparatively higher than the other water samples. However, the value was within the permissible limit. The sulfate content of all water samples was within the limit. The prescribed limit of sulfate is 200 mg/l.

The BOD and COD of different water samples are shown in figure 5.7.

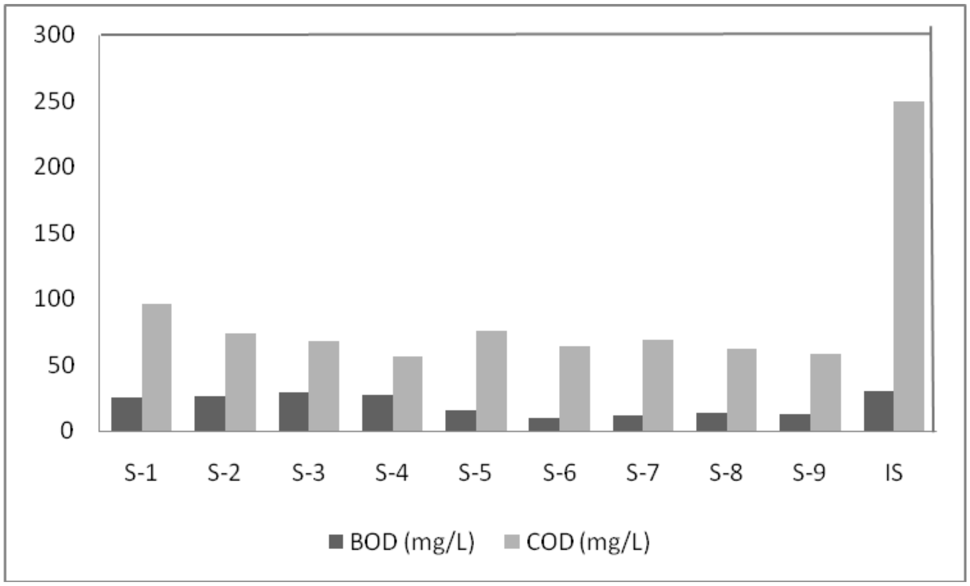

Figure 5.7: BOD and COD of different water samples

It may be observed from table 4.6 and figure 5.7 that the Biological oxygen demand (BOD) of the water samples ranged from 10 to 29 mg/l in the study area. The BOD of S-1, S-2, S-3 and S-4 was comparatively higher than the other water samples. The BOD of S-3 was highest among the water samples. However, the values were within the permissible limit. The BOD of S-6 was lowest among all the water samples. The prescribed limit of BOD is 30 mg/l.

The COD of the water samples ranged from 56 to 96 mg/l in the study area. The COD of all water samples were within the permissible limit. The prescribed limit of COD is 250 mg/l.

5.2 CONCLUSION

Due to rapid industrialization and modernization, the coal-based industries are increasing at an alarming rate. The coal based industries, such as by-product coke-plants, coal washeries and thermal power plants release their liquid effluents, which are needed urgent attention for the treatment, before they are discharged into the fresh water streams. The impact of fluoride pollution is severe in the belt of Angul-Talcher, Orissa. Incidence of white spots all over the body, incurable skin infections and lumps of dead skin are increasing among the population. A high percentage of gastro- intestinal parasitic infection was found in the fecal samples of cattle in the villages affected by effluents from coal based industries and coal mining.

Hence water quality studies are very essential for rational planning of pollution control strategies and their prioritization, to assess nature and extent of pollution control needed in different water bodies or their part, to evaluate water quality trend over a period of time and to assess assimilative capacity of a water body thereby reducing cost on pollution control.

In this present work, water samples were collected from three coal based industries namely NALCO, Angul, Rourkela Steel Plant, Rourkela and NTPC, Talcher. A careful study into table and figure reveals the water quality of water samples S-1, S-2, S-3 and S-4 with respect to alkalinity, aluminum, arsenic, calcium, color, COD and conductivity was meeting the desired criteria. The sample S-3 had a very high BOD and hardness value followed by S-4, S-2 and S-1. The water sample S-5 had a very high content of fluoride, turbidity, conductivity, arsenic, iron and hardness in comparison to other samples. The sample S-8 had a very high content of fluoride, conductivity and arsenic in comparison to S-9. The water sample S-3 from Nalco Ash Pond and S-5 from RSP, Rourkela were comparatively more polluted than other water samples.

With alarming increase of surface water pollution, it becomes very much essential for the Orissa Government and Orissa Pollution Control Board (OPCB) to control further pollution of the surface water and deterioration in water quality. The overall management is necessary and Central Pollution Control Board (CPCB)/ State Pollution Control Board (SPCB) rules should be strictly implemented. Educating the urban as well as the rural mass is another major step to put a check on the surface water pollution.

CHAPTER

6

REFERENCES

6. REFERENCES

American Public Health Association (APHA),1985, Standards Methods for Examination of Water and Wastewater, 16th Edition, United States of America, Baltimore, Maryland.

Baba, A., Kaya, A. and Birsoy Y.K., 2003, “The Effect of Yatagan Thermal Power Plant (Mugla, Turkey) on the Quality of Surface and Ground Waters”, *Water, Air and Soil Pollution*. Volume 14, Nos.1-4, pp. 93-111.

Bates, R.G., 1973, Determination of pH, theory and practice, 2nd Edition, John Wiley and Sons, New York.

Bishnoi, M. and Malik, R., 2008 “Ground water quality in environmentally degraded localities of Panipat city, India”, *Journal of Environmental Biology*. Volume 29, No.6, pp. 881-886.

CCME., 2001. Canadian water quality guidelines for the protection of aquatic life: CCME Water Quality Index 1.0, User’s manual. In: *Canadian Environmental quality guidelines,* 1999, Canadian Council of Ministers of the Environment, Winnipeg, Manitoba.

Central Board for the Prevention and Control of Water Pollution, 1979, Scheme for Zoning and Classification of Indian Rivers, Estuaries and Coastal Waters (Part One: Sweet Water) New Delhi , pp. 1-19.

Central Pollution Control Board(CPCB), 2003, Water Quality in India Status and Trend (1990-2001), pp. 1-17

Erbe, M.W., Keating, R.W. and Hodges, W.K., 2003, “Evaluation of Water Quality Conditions Associated with the Use of Coal Combustion Products for Highway Embankments”, *Environmental Protection Agency*. Case Study 9, pp. 1-10.

Genderen, E.V., Adams, W., Sprang, P.V. and Arnold, R., 2009, “An evaluation of the bioavailability and aquatic toxicity attributed to ambient copper concentrations in surface waters from several parts of the world”, Integrated Environmental Assessment and Management. Volume 4, pp. 416-424.

Howard, C.S., 1993 “Determination of total dissolved solids in water analysis”, *Ind. Eng. Chem., Analysis,* Ed. 5:4

Jambrik, R. and Bartha, M., 1994, “Ground Water Quality Affected by Mining in the East Borsod Brown Coal Basin, Hungary”, *Mine Water and the Environment*. Volume 13, pp. 49-58.

Junshum, P., Traichaiyapom, S. and Chunluchanon, S., 2004, ‘Water Quality at the Mae Moh Power Plant, Lampang Province”, *International Journal of Environmental Science and Technology*. Volume 29, No.2, pp. 51-54.

Kar, D., Sur, P., Mandal, S.K., Saha, T. and Kole, R.K., 2008, “Assessment of heavy metal pollution in surface water”, *International Journal of Environmental Science*. Volume 5, No.1, pp. 119-124.

Knight, A.G., 1951," The photometric estimate of color in turbid waters", *J.Inst. Water Eng*., pp. 23-56

Kuipers, James R., 2008, "The Effects of Coal Bed Methane Production on Surface and Ground Water Resources", *Meeting on the Status of Data and Management Regarding the Effects of Coal Bed Methane Production on Surface and Ground Water Resources*. Adam's Mark Hotel-Denver, 1550 Court Place, Denver, Colorado.

Lind, J.E., Zwolenik J.J. and Fuoss R.M., 1959, Calibration of conductance cells at 25 C, *J. Amer. Chem. Soc*. 81:1557

Mohlman, F.W., Hurzwitz E., Barnett G.R and Ramer H.K., 1946, Modernization of the BOD test for determining the efficiency of the sewage treatment process, *Sewage Works J*., 18:1113.

Nollet, L. M. L., 2007, "Handbook of water analysis", Chapter-1, Sampling Methods in Surface Waters, CRC Press, Second Edition, pp. 2-15

Parashar, C.; Dixit, S. and Shrivastava, R., 2007, "Assessment of Possible Impacts of Climate Change in Water Reservoir of Bhopal with Special Reference to Heavy Metals, Central Region – India", *J. Appl. Sci. Environ. Manage.* Volume 11, No.2, pp. 91-93

Qian, Y., Migliaccio, K.W. and Wan, Y., 2007 "Surface water quality evaluation using multivariate methods and a new water quality index in the Indian River Lagoon, Florida", *Water Resources Research.* Volume 13, pp.1-10.

Sawyer, C.N., P. Callejas, M. Moore and A.Q.Y. Tom, 1950, Primary Standards for BOD work, Sewage Ind. Wastes, pp. 22-26.

Segar, D.A. and J.G. Gonzalez, 1972, Evaluation of atomic absorption with a heated graphite atomizer for the direct determination of trace transition metals in sea water, Anal. Chim. Acta, pp. 45-68

Singh, G., 1990, "Status of Water Quality in a Coal Mining Environment", *Jr. Ind. Poll. Cont*. Volume 6, No.2, pp. 69-76.

Tiri., A. and Boudoukha, A., 2010, " Hydrochemical Analysis and Assessment of Surface Water Quality in Koudiat Medouar Reservoir, Algeria", *European Journal of Scientific Research.* Volume 41, No. 2, pp. 273-285.

Tiwary, R.K. and Dhar, B.B., 1994, "Environmental Pollution from Coal Mining Activities in Damodar River Basin, India", *Mine Water and Environment.* Volume 13, pp. 1-10.

Whipple, G.C. and Jackson D.D, 1990, A comparative study of the methods used for the measurement of turbidity of water, Mass. Inst. Technol. Quart. pp. 1-13.

Xing Mian, 2010, "Study on the Water Conservation Management Measures in Thermal Power Plants", *International Journal of Business Management.* Volume 5, No.3, pp. 16-164.