INDUSTRIAL WATER ANALYSIS HANDBOOK

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DEDICATED

TO

THE LOTUS FEET OF

LORD MURUGA

AND TO MY PARENTS

C.K.NATARAJ & ARUNAGIRI AMMAL

I gratefully acknowledge,

1) American Public Health Association, Washington

2) American Society for Testing and Materials, Philadelphia

3) International Organization for Standardization, Switzerland

4) Hach Company, Loveland, Colorado, U.S.A

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- N.MANIVASAKAM

PREFACE

Water analysis has become extremely important for many reasons. Not only to design suitable water treatment plant during commissioning of the industry but it is essential for continuous monitoring of the quality of treated water. Without a proper water analysis program, the efficacy of water treatment cannot be ascertained. A proper water analysis would also reduce the cost on treatment significantly. Knowing this fully well, every industry is setting up their own water analysis laboratory as a part of their industry. Abundant literature is available on the analysis of water, but this book is especially written to suit the needs of industries. All the test procedures for the parameters pertaining to industrial water analysis are provided in this book and discussed in detail. Another salient feature of this book is that the analytical procedures are given in a step by step way so that it becomes easier for the analyst to carryout analysis of water. Chapters are arranged in alphabetical order for easy access to the required chapter. Thus this book would serve as a valuable reference to carryout analysis of water for any intended industrial purpose. This apart, it is extremely useful to carryout examination of waster water too.

This book is divided into four parts.

Part – I 'Introduction' provides a detailed introduction on analysis of water along with parameters to be determined for each industrial use, thus helps to reduce the time required for analysis and labor involved in analysis.

In Part – II 'Chemical Analysis', elaborate testing procedures for all the parameters necessary for industrial uses are given. Exclusive chapters in the beginning on 'Sampling of water' and 'Sampling of Boiler water' will provide the analyst a detailed sampling program and the important sampling points so that the analysis would be more meaningful and more useful. Detailed analytical procedures for 65 chemical parameters are given which makes this book a handy reference for carrying out analysis without any difficulty.

Part – III 'Microbiological Analysis' deals with the identification and determination of the density of microbial organisms that are likely to interfere in industrial processes. To aid the analyst, separate chapters starting from the Requirement of Chemicals, Glassware and Equipment, Technics involved in

Microbiological Analysis, Sampling of Water for Microbiological Examination and Preparation of Media and Reagents, to identification of specific organisms are provided with a detailed discussion.

In Part – IV 'Microscopical Examination', a brief account of microscopical organisms is given. The common organisms present in water along with their habitat and significance are also dealt.

This book would serve as a handy reference to all wet processing industries. This book would be helpful in multifarious ways to Analysts, Chemists, Engineers, and Managers of industries and Water Treatment Consultants, Firms engaged in Water Treatment and other personnel engaged in water analysis and water treatment. This apart, this book would also be a source book to students of Industrial Engineering, Chemical Engineering, Industrial Chemistry, Applied chemistry, Environmental Engineering and Environmental Science and other allied faculties of Colleges and Universities.

This book has been prepared with the help and assistance of a number of people. Their assistance made this book a most useful volume. I owe a great debt of gratitude to all of them. Some of the organizations have been most gracious in granting permission to reproduce certain illustrations, figures and portions from their publications. Their cooperation is gratefully acknowledged. A special debt of gratitude is due to M/S. Chemical Publishing Company, Gloucester, U.S.A., for their keen interest shown towards the publication of this book.

Comments and criticisms as well as suggestions for the improvement of the book are solicited.

Coimbatore – 42 (TN) **- N.MANIVASAKAM**
India.

This book is divided into the following parts.

Part I. ***INTRODUCTION***

Part II. ***CHEMICAL ANALYSIS***

Part III. ***MICROBIOLOGICAL ANALYSIS***

Part IV. ***MICROSCOPICAL EXAMINATION***

CONTENTS

PART I

INTRODUCTION

CHAPTER - 1
INTRODUCTION

Water analysis has become increasingly important for many reasons. Water is the material that is widely employed in industries in multifarious ways – water is the raw material, water is the ingredient, water is the medium of reaction, water is the conveying medium, water is used for washing, water is used to generate steam and it is the major cooling agent and so on. For each and every industrial use, the quality of water is very important and it is the judging factor of the quality of finished product as well as the criterion for protecting boilers, cooling systems, machineries and equipments from scale formation and corrosion. Water analysis is the key component in designing suitable water treatment plant and to maintain the water quality. Without a proper water analysis program, the efficacy of water treatment cannot be ascertained. A proper water analysis would also reduce the cost on treatment considerably. Since each industrial use needs a water of specific quality, a detailed analysis is essential to know the quality of water available and to apply suitable treatment to render the water fit for the specific purpose and to maintain the same.

Analysis of water includes four components namely,

1. *Chemical Analysis*
2. *Microbiological Analysis*
3. *Microscopical Examination*
4. *Testing for Radioactivity*

CHEMICAL ANALYSIS

Examination for physical characteristics and chemical composition together called as 'Chemical Analysis'. All the parameters that comes under chemical analysis are listed below.

Physical Properties	Metals	Non-metallics	Dissolved Gases	Organics	Other Tests
Color	Aluminium	Acidity	Carbon - dioxide	Hydrazine	BOD
Electrical Conductivity	Arsenic	Alkalinity	Chlorine (Residual)	Nitrogen (Ammonia)	Calcium carbonate Stability Test
Odor	Boron	Chloride	Oxygen (Dissolved)	Nitrogen (Albuminoid)	Chlorine demand
pH Value	Cadmium	Cyanide		Nitrogen (Organic)	Coagulant demand
Solids	Calcium	Fluoride		Nitrogen (Total Kjeldahl)	COD
- Total	Chromium	Iodide		Oil and grease	Equivalent Mineral Acidity
- Dissolved	Copper	Nitrate		Phenols	Langellier Index
- Suspended	Hardness	Nitrite		Surfactants	Particle Counting
- Settleable	Iron	Phosphate		Tannin and Lignin	Permanganate Value
Temperature	Lead	Silica		Volatile acids	Residual Sodium Carbonate
Turbidity	Magnesium	Sulfate			Silt Density Index
	Manganese	Sulfide			Sodium - Adsorption Ratio
	Mercury	Sulfite			Sodium Slip
	Nickel				
	Potassium				
	Selenium				
	Sodium				
	Silver				
	Zinc				

MICROBIOLOGICAL ANALYSIS

Microbiological analysis is carried out to detect the presence and density of microbial organisms in water. These organisms may render the water unsuitable in one or other way for the intended use, especially for food industries, pharmaceutical industries, fermentation industries and electronics industries. Hence is it essential that the water used in industries should also be free from microorganisms. In this book, procedures for the following organisms, are given.

1. *Standard Plant Count (To detect the number of viable micro-organisms present in water)*
2. *Coliform bacteria (To detect fecal contamination)*
3. *Fecal coliforms (Escherichia coli) (To detect fecal contamination)*
4. *Proteolytic Bacteria (Protein degrading bacteria. Essential test for Food Industries)*
5. *Lipolytic Bacteria (Lipid degrading bacteria. Essential test for Food Industries)*
6. *Thermophilic Bacteria (To be tested for water used in Dairy)*
7. *Gelatin Liquefying Bacteria*
8. *Iron Bacteria*
9. *Sulfate-Reducing Bacteria*
10. *Sulfur-Oxidizing Bacteria*
11. *Yeast and Mould*
12. *Slime Forming Organisms*

See Part – III, 'MICROBIOLOGICAL ANALYSIS' for more details

MICROSCOPICAL EXAMINATION

Water may contain numerous minute organisms that could be detected only under microscope. Many industrial processes virtually require water free of such microscopical organisms, as they impart color, odor and turbidity to water. Some of the higher forms may affect the health also. A detailed microscopical examination will reveal the presence and concentration of phytoplanktons such as algae, diatoms, flagellates and zooplanktons such as protozoans, ciliated protozoans, rotifers, crustaceans and other forms. For details, refer Part – IV, 'MICROSCOPICAL EXAMINATION'.

TESTS FOR RADIO ACTIVITY

Radio active materials find their way into water courses mainly from the discharge of waste water from nuclear power plants and due to extensive use of radio tracers. They are highly undesirable in processing industries. Stringent limits for radio active materials are stipulated for drinking water and water used for food processing and fermentation industries. Water used in these industries must comply with these requirements. Radio active measurements are helpful to detect the radio active contamination and contaminant levels in water.

ANALYSIS OF RAW WATER & TREATED WATER

The primary objective of the analysis of raw water in industries is to find out its quality to design a suitable treatment plant and to plan a treatment program. Detailed analysis is necessary to design an effective and comprehensive treatment plant. Seasonal variations and corresponding fluctuations* in raw water quality have to be taken into account while designing a treatment plant. If two or more sources with plenty of water are available, raw water analysis would help to select the source to which minimum treatment is required. Such selection would result in considerable savings in treatment costs and in the subsequent control analysis.

After the treatment plant is installed, the treated water has to be tested periodically. The periodicity (hourly, daily, weekly etc.,) is dependent on the industrial purpose for which the water is used and the type of treatment plant installed. The treated waters are tested to find out the efficacy, uniformity and consistency of treatment. Any over treatment will lead to unnecessary expenditure and under treatment would result in poor quality water and consequently lead to equipment failure and / or inferior product.

* Throughout the world, rivers are the most commonly used water sources for industrial purposes. Since they are subject to pollution by industries, sewage, agricultural run-off and other man made activities, considerable variation in the concentration of many constituents should be anticipated along with variations due to seasonal changes. Whereas ground waters are essentially constant in composition and there may not be much variation in quality characteristics.

ANALYTICAL PROGRAM

Drawing an analytical program is highly imperative to attain the objective of the best performance of the treatment system and securing water of desired quality for the particular industrial use and maintaining the treatment. The basic components of an analytical program are,

i. Fixing the sampling points [(i.e) the stages of treatment system that need control]
ii. Frequency of sampling
iii. Parameters to be determined [(i.e) constituents that affect the process at the particular stage]
iv. Method of analysis.

All these components are entirely dependent on the quality requirement of water for the intended industrial use and the type of treatment plants installed.

While planning the program of sampling and analysis, care should be exercised that the program should not be too extensive incorporating unnecessary data which involve then more labour and also expensive and wastage of time. Similarly an inadequate program would lead to improper conclusions and improper treatment resulting in poor quality products and damage to equipments. The best program is the one with minimum sampling points and tests, at the same time providing necessary information. Regular analyses for raw water, treated water used in process have to be carried out. Analysis of condensate returns and recirculating cooling water is also necessary.

Most of the industries require testing of water, only to asses the physical characteristics and chemical composition. Some other industrial processes need water of satisfactory bacteriological quality also (eg) food industries, fermentation industries and electronics industries. In such cases, both chemical and bacteriological analysis need to be carried out. When the water is susceptible to radio active contamination, it has to be tested for radio activity also.

In Chapter - 2, the parameters that need to be determined are given industry wise and may be referred for further information. For fixing the right sampling points refer Chapter - 5, 'SAMPLING OF WATER FOR CHEMICAL ANALYSIS' and Chapter - 6 'SAMPLING OF BOILER WATER'. For detailed analytical procedures refer Part – II and Part – III.

CHAPTER – 2

PARAMETERS TO BE DETERMINED

(INDUSTRY WISE)

Given below is the list of parameters to be tested on a regular basis. To aid the analyst the list is given industry wise. These are the minimum tests to be carried out regularly which are also termed as 'Control Tests'. Even among these, if some of the parameters remain constant and exhibit no variation, they need not be done. It is reiterated however, while commissioning the industry the water has to be tested for all parameters to assess its suitability for the particular industrial use and to design a suitable treatment plant. If surface waters are used, their characteristics have to be studied seasonally prior to designing treatment plant. In addition to the control parameters, they have to be checked for other parameters also when they are suspected to vary in character due to seasonal variations and/or pollution from upstream side.

The present day softeners, demineralizers, reverse osmosis plants and steam generation systems are equipped with fully automatic (or semiautomatic) continuous analyzers which measure the pH, temperature, turbidity conductivity, hardness, dissolved oxygen and silica. A schematic diagram of water treatment plants and steam generating equipments along with continuous analyzers are depicted in Fig. 2 – 1. Needless to say that in addition to such measurements, a testing schedule has to be established to make sure that sufficient information is obtained with the minimum number of tests. Such schedules and control parameters are described in the following sections.

CONTROL PARAMETERS FOR TREATMENT PROCESSES

Lime – Soda Softening

1. **pH value :** Continuous analysis is desirable
2. **Hardness:** May be tested once per shift
3. **Phosphate:** For a significant reduction of hardness, phosphate is usually added in hot lime-soda softening. Maintenance of a residual of 6 – 8 ppm is necessary. May be tested once per shift.

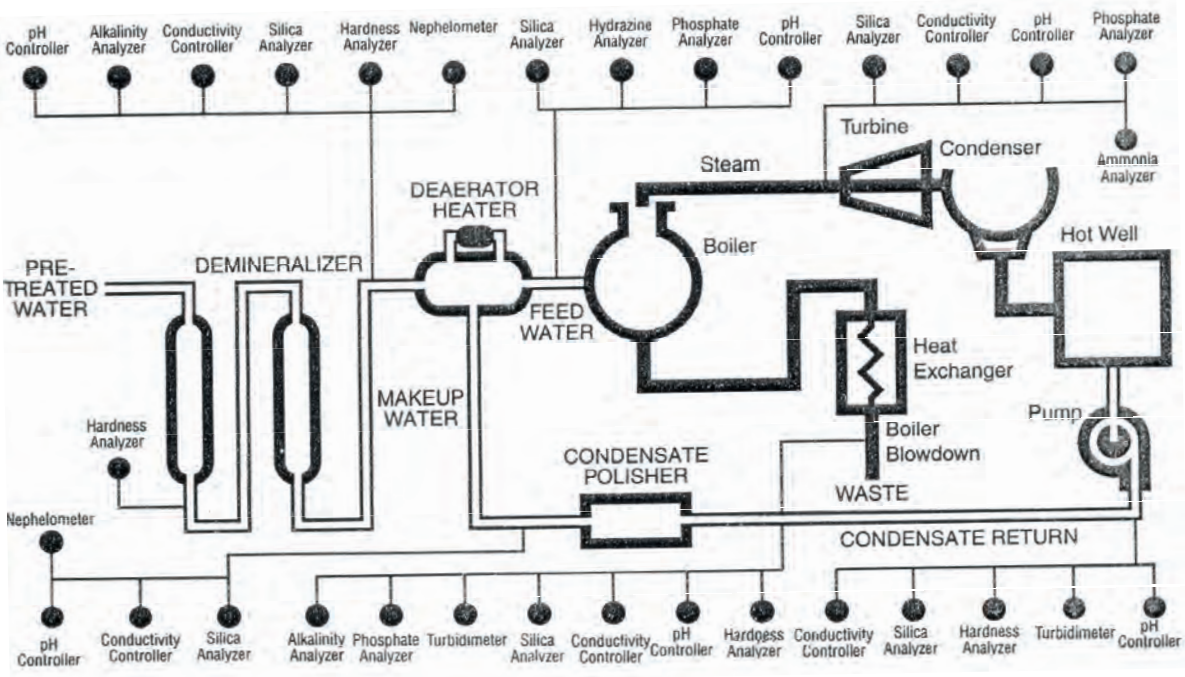

Fig. 2 – 1. Water Treatment Plants and steam Generation Systems Continuous Analyzers and Strategic Points at which they are installed*.

Cation – exchange Softening

1. **pH value:** Continuous analysis is desirable.

2. **Hardness:** A continuous analyzer for hardness is convenient for monitoring the performance of cation exchangers. The instrument is normally installed on the softener outlet header. When it alarms, the softened water must be checked for leakage of hardness. EDTA titric metric method is recommended for checking. (In the absence of a continuous analyzer, the softened water should be checked for hardness every 2 hr.)

* Fig. 2 – 1 is reproduced with the kind permission from M/s. Hach Company, Colorado, U.S.A., from their publication, "Hach Water Analysis Hand Book" 4th Edition (Revision – 2) – 2003.

Demineralization

1. Conductivity
2. pH value
3. Silica
4. Hardness
5. Sodium
6. Alkalinity
7. Turbidity.

The Demineralizers are usually installed with continuous analyzers for monitoring pH and conductivity. Both conductivity and pH measurements are used to indicate breakthrough in demineralization. As the resin becomes exhausted, the pH falls and the conductivity rises.

In normal operation, the pH of the anion exchanger effluent is about 8. If the pH becomes 9 or more it is an indication of excessive sodium ion leakage from the cation exchanger. The present day trend is to install a continuous analyzer for sodium in the cation exchanger outlet so that sodium leakage could be immediately known.

Automatic silica analyzers are also installed at the anion exchanger outlet. When demineralizers approach exhaustion, silica is the first impurity to breakthrough into the effluent. Due to its low ionic strength, silica cannot be detected readily by conductivity meters. However automatic analyzers are capable of detecting increasing levels of silica that occur before complete exhaustion. Regeneration can then be initiated.

CONTROL PARAMETES FOR STEAM GENERATION SYSTEMS

Feed Water

Boiler feed water is a mixture of condensate and makeup water. Usually condensate will be in high proportion (ranging from 95% to 99% - sometimes total feed water is condensate) and make up will be in a lower proportion. Before feeding, the quality must be known in order to protect the boiler system from scaling and corrosion. Detailed analysis may be carried out at suitable intervals. However, all the parameters need not be done daily. A few

control tests alone have to be done which clearly give a picture on the quality of feed water. Necessary control parameters are tabulated (See Table 2 – 1)

Boiler Water

The analysis of boiler water is extremely useful in detecting the conditions inside the boiler and to detect under or over treatment. Based on the analysis of boiler water, dosage of chemicals can be controlled. In this case also certain chemical parameters have to be checked frequently which are given in Table 2 – 2.

Steam

It is extremely important to determine the purity of steam frequently. Needless to say that steam purity is affected by certain operating variables and therefore it is best to sample and monitor continuously the quality of steam. Unlike with other samples, obtaining a representative sample of steam is very difficult and hence several precautions need to be observed. Purity of steam is determined by measuring either the conductivity or sodium concentration in a condensed sample. For a detailed analytical procedure refer, chapter – 76.

Condensate

Condensate is nothing but the condensed steam and is a water of extreme purity. The condensate return system is a revealing sampling point to monitor total boiler water treatment performance. The parameters, turbidity, electrical conductivity and hardness are used to find out in-leakage through heat exchangers and condensers. If the conductivity of the combined condensate rises, individual returned streams should be checked for hardness. Test for silica also may be carried out on such return streams to detect contamination. Regular measurement of the pH of the condensate is necessary to regulate the dosage of amines. (After the addition of neutralizing amines the pH should be in the range of 8 – 9). Tests for iron, copper and dissolved oxygen are carried out to detect corrosion problems. Silica and sodium are important parameters which indicate carryover problems and / or condenser leakage (see Table 2 – 3). As indicated already, continuous analyzers are available for the measurement of sodium as low as 0.1 ppb. The major advantage with these analyzers is that these instruments suffer no interference from hydrazine, morpholine, cyclohexylamine or ammonia.

Blow Down

Blowing down is an essential operation in any boiler water treatment program. Blowdown removes precipitated sludge and dissolved solids from the boiler before harmful levels are reached. Blowdown can be continuous or intermittent. In either case, analysis is required to maintain the critical balance between solids removal and the loss of heat and treatment chemicals that must be replaced. The control parameters are listed below. (See Table 2 – 4).

Raw Water

Raw waters have also to be tested occasionally to detect any variations in quality. Ground waters normally do not show any variations. Surface waters, however are subject to fluctuations in quality due to seasonal variations and/or pollution from upstream side and may require frequent checking.

TABLE 2–1

BOILER FEED WATERS – CONTROL PARAMETERS AND TESTING SCHEDULE

Sl.No.	Parameter	Frequency
1.	Electrical Conductivity	Continuously
2.	pH value	- do -
3.	Total Hardness	Daily
4.	Total Alkalinity	- do -
5.	Chloride	Once per shift (i.e., once in 8 hrs)
6.	Silica	- do -
7.	Dissolved Oxygen	- do -
8.	Residual Sodium sulfite / Hydrazine	- do -
9.	Phosphate	Need to be done only if the water is softened by Lime – Soda process. Once per day.
10.	Iron	Occasionally
11.	Copper	- do -
12.	Oil	- do -

TABLE 2–2

BOILER WATER - CONTROL PARAMETERS AND TESTING SCHEDULE

Sl.No.	Parameter	Frequency
1.	pH value	Continuously
2.	Total Hardness	Once per shift (once in 8 hrs)
3.	Total Alkalinity	- do -
4.	Caustic Alkalinity	- do -
5.	Chloride	- do -
6.	Silica	- do -
7.	Dissolved Oxygen	Continuously
8.	Residual Sodium sulfite / Hydrazine	Once per shift
9.	Phosphate	- do -
10.	Iron	- do -
11.	Copper	- do -
12.	Oil	Occassionally
13.	Residual Chelant	Once per day

TABLE 2–3

CONDENSATE–CONTROL PARAMETERS AND TESTING SCHEDULE

Sl.No.	Parameter	Frequency
1.	Turbidity	Once per day
2.	Electrical conductivity	Continuously
3.	pH value	- do -
4.	Total Hardness	Once per day
5.	Silica	- do -
6.	Sodium	- do -
7.	Iron	- do -
8.	Copper	- do -
9.	Oil	- do -

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