CHEMICAL ANALYSIS OF NATURAL AND INDUSTRIAL WASTE WATERS

A Thesis presented to the Ahmadu Bello University, Zaria in partial fulfillment for the Award of the Degree of Master of Science in Analytical Chemistry.

By

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DECLARATION

"Chemical Analysis of Natural and Industrial Waste waters" is wholly my work and has not been part of any presentation for any other qualifications.

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ABSTRACT

The present analytical studies had been carried out on various samples of water such as raw and treated waters in Kaduna and Zaria, three wells in Samaru, and industrial effluents from Federal Superphosphate Fertilizers Company, Kaduna, Nortex Nigerian Limited Kaduna, and Nigerian Holts Tanneries, Kano, the three typical representative industries from the Northern part of this country.

Based on the analytical data collected an attempt has been made

(a) to assess the suitability of the treated water for drinking and washing purposes

(b) to assess the extent of pollution caused to river Kaduna as a result of industrial waste water discharges in it

(c) to compare the results with the existing International standards for water quality.

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CHAPTER I

INTRODUCTION

In addition to air, water is essential for human beings, animals and plants. It is believed that man can survive without food for several weeks but in the absence of water death results in a few days. We need water not only for drinking but also in our daily use for sanitation purposes, e.g. in washing the body, clothes and other house-hold articles.

Large quantity of water is used in irrigation, as a cooling and rinsing agent, as a raw material and for generation of energies.

It is not surprising therefore that the supply of water is often a decisive factor in the lifestyle of every society.

The Federal Government of Nigeria attaches great importance to supply of water for drinking irrigation and industries by establishing the Ministry of Water Resources.

Besides the quantity of waters needed the quality of water is of paramount importance. The increasing realisation of the effect of contaminants both organic

and inorganic on city and local water supplies and the history's record from the hospitals of the devastating nature of epidemics due to water borne diseases may necessitate a careful and detailed analysis of water for its sanitary value and for the development of ways and means to fight and eliminate such contamination. This when achieved may enhance the chances of safety to the public health.

A need for physical, chemical and bacteriological analysis of water supplies becomes evident when one considers the fact that water is never found pure in nature.[1] The nearest approach to pure water is rain water which contains small amounts of organic matter and some dissolved gases absorbed during its passage through the atmosphere.

Chemically pure water would be undesirable in nature since natural living organisms would have no life without dissolved oxygen. Such a water would not be healthy for drinking without a certain minimum mineral content. However the secondary components which reduce the consumption value of water are much more numerous. The nature of ground over and through which water flows determines the soluble impurities.

These include mineral salts such as carbonates, sulphates and chlorides, etc. In addition surface waters such as rivers, lakes and ponds contain suspended solids and bacteria derived from sewage, plants and industrial wastes.

With the above factors in view it is not always possible to supply such a water directly to the consumers without a thorough analysis ascertaining the presence of various components and their extent.

Objective of the Work:

Chemical analysis of water is an aspect of analytical studies of our environments[2] and studies like this may be made to evaluate nuisance effects and economic factors associated with corrosion, staining and damage to plants and animal life. It is however important to note that many elements that may be regarded as pollutants may be essential elements in trace amounts.

This analytical study has been carried out (a) to determine the presence of undesirable element or compound in water that might be detrimental to health if used for drinking purposes, or causing undesirable effects when used for industrial purposes.

(b) to gain information as to whether or not the treated waters supplied to consumers comply with International standards for water quality.[3] Unfortunately there is no standard set for this country in terms of drinking water as yet.

(c) The study is also aimed at gathering information about the possible pollution caused by industrial wastewaters.

(d) Besides these mentioned objectives the study has afforded me a lot of opportunity as a prospective analytical chemist in carrying out diverse analyses especially in determination of trace elements in the presence of high concentrations of different elements and various interferring components.

In a developing economy like Nigeria the processes of production and consumption yield vast amounts of residual wastematerials. Disposal of these materials has important implications for the community health, well being and quality of life and this can present a problem of great social significance. Water has long been used as a medium for disposal and assimilation of wastes.

In the present standards of water quality chemical analysis has a tremendous role to play. Any appreciation of present day chemical analysis must be based upon the knowledge that natural waters are of complex character containing suspended matter, and a large number of dissolved substances, many in minute but significant concentrations.[3,4] Due to this complexity even the most comprehensive chemical analysis cannot disclose concentrations of all its constituents. Chemical analysis should therefore be directed towards specific ends, bringing the various mineral, sanitary and spectrographic tests to bear upon the empirical solution of problems of our environment. An example of this approach is the well established determination of colour, turbidity, ammonia, nitrates, oxygen consumed values, hardness, alkalinity etc. The above series of determinations are designed specifically to reveal the general character of the water, to indicate whether or not the supply had been exposed to pollution of public health significance as shown by the character and concentration of organic matter and to answer such practical questions as that of the best level from which to secure water in a reservoir.

Another illustrations of this specific approach are the analyses directed towards the appraisal of chemical quality from the standpoint of controlling water purification processes e.g. determination of residual chlorine, turbidity, hardness, alkalinity, P^H value and iron content.

Iron, copper, zinc and lead are often present in portable water supplies incidental to corrosive action of the water itself. Because these constituents have specific sanitary significance provision for their control should be made in standards of water quality. Such tables are shown in the (appendix A & B).

Toxic Chemicals in Water:

The toxicity of chemicals in water is dictated by several factors including nature, stability and concentration of the chemical dosage, synergistic and antagonistic behaviour of the toxicant in association with other agents and the cumulative effects due to the concentration of the toxicant in biological tissues. Because of the variability and multiplicity of these factors, it is necessary to allow a reasonable safety factor for determining quantitative criteria for toxicants in drinking water. In ideal situations

the use of water containing any toxicant should not be permitted but because wastewaters containing toxic substances have and are still being discharged to water sources, water completely devoid of toxicants is only rarely found. Even when wastewaters are completely excluded from drinking water sources, toxicants enter through rainfall, natural leaching, aerial spraying of pesticides or agricultural land run off.[5]

With increasing analyses of water criteria for toxicants in water both for short and long terms exposure may emerge. It is difficult however to draw a line of distinction from available data what proportions of the dosage are contributed by various sources or media (air, water or food) because exposure to polluted air, water consumption and daily food intake vary considerably.

The scope and limitations of the present work have been on the examinations of the following tests and their sanitary significance in drinking water, raw water, well waters and industrial wastewaters.

1.1 Electrical Conductivity

This is a measure of ability of solution to carry electrical current and this depends on the number and type of ions present in solution. The determination of electrical conductivity is becoming a matter of routine analysis since results obtained from it are a very useful check on chemical analysis and often save the estimation of total dissolved solids.

1.2 P^H Value

The P^H values of most natural waters fall within the range 6 to 9. Majority of waters are slightly basic due to the presence of carbonate and bicarbonate.

P^H adjustment in the treatment plant effluents helps in controlling corrosion in the distribution systems.[4]

1.3 Turbidity

This may be interpreted as a lack of clarity or brilliance in water, but should not be confused with colour, because it is possible for water to be dark in colour and yet clear and not turbid. It is an optical measurement based on the interference sustained by rays of light passing through a water sample.

Sanitary significance

Turbidity interferes with the efficiency of disinfection process especially in cases where turbidity is caused by sewage solids many of the pathogenic organisms may be encased in the particles and protected from the disinfectant.[6] Consumers of public water supplies detest turbidity in water. Any turbidity in drinking water is automatically associated with possible contamination or sewage pollution and health hazard occasioned by it.

Colour and odour are aesthetically objectionable in drinking waters. Tastes are aesthetically undesirable though generally of no sanitary significance except for laxative effects produced when dissolved solids become too excessive.

1,4 Temperature

Temperature of the sample is normally recorded at the time of collection. Water temperatures at different depths in reservoirs are required in limnologic studies. It is possible to employ temperature readings in the calculation of various forms of alkalinity and in saturation and stability studies with respect to calcium carbonate.[7]

1.5 Ammonia

This is a non persistent and non-cumulative toxic substance, the toxicity to aquatic life depends upon the P^H value and dissolved oxygen concentration of the water Ammonia has been shown to be lethal to fish probably because it decreases the oxygen carrying capacity of the blood.[8] It is recommended that the derived working level of ammonia in waters supporting aquatic life should be 0.1 mg.[5]

1.6 Hardness

This is the term used to express the soap destroying properties of water. The main compounds responsible for hardness are calcium and magnesium sulphates and chlorides, though hardness may be caused by other polyvalent ions such as aluminium, iron, manganese etc. but these often exist in insignificant concentrations. Hardness is not a hazard to health and hence is not included in standards of water quality, although an inverse statistical correlation between water hardness (as a characteristic) and certain types of cardiovascular diseases has been shown, the exact relationship is still under investigation.[5]

1.7 Alkalinity

It is a measure of hydroxide, normal carbonate and bicarbonate content of water. In natural water these are usually present as compounds of potassium, sodium, calcium or magnesium.

Abnormally high increase in alkalinity over that of the public water supply or stream involved may indicate the entry of a strong basic industrial water.

Sanitary significance

In moderate concentrations alkalinity in drinking water has no health significance. Highly alkaline waters are usually unpalatable and consumers tend to seek other supplies.

1.8 Chlorides

Occurs in all natural waters in widely varying concentrations. The chloride content normally increases as the mineral content increases.

Many industrial wastes contain appreciable amounts of chlorides. Chlorides in reasonable concentrations are not harmful to humans. At concentrations above 250mg/l they give a salty taste to water which is objectionable to many people. In many areas of the world where supplies are scarce,

sources containing as much as 200 mg/l are used for domestic purposes without adverse effects once human system becomes used to the water.[5,7.]

1.9 Residual Chlorine

Occurs in water as a result of treatment process. Chlorine is used as a disinfectant in destroying micro-organisms and its efficiency depends on its concentration and time of contact. Longer time of contact is preferred hence the application of ammonia - chlorine (chloramine) process in some waterworks.

1.10 Dissolved Oxygen

The levels of dissolved oxygen in natural and waste waters are depended on the physical, chemical and biochemical activities prevailing in the water body. The solubility of atmospheric oxygen in fresh waters ranges from 14.6 mg/l at $0^{o}C$ to about 7 mg/l at $35^{o}C$.[9] The low solubility of oxygen in waters is a major factor that limits the purification capacity of natural waters.

Analysis of dissolved oxygen is a key test in water pollution control. Adequate dissolved oxygen is necessary for the life of fish and other aquatic organisms. Dissolved oxygen measurements are vital

for maintaining aerobic conditions in natural waters, that receive pollutional matter and aerobic treatment processes intended to purify domestic industrial wastewaters. Oxygen is a significant factor in the corrosion of iron and steel particularly in water distribution system and in steam boilers.[6,9]

1.11 Biochemical oxygen Demand (BOD)

It is a measure of amount of oxygen required to oxidise organic matter by bacterial action. BOD test is widely applied in measuring waste loading to treatment i.e. to determine the pollutional strength of sewages and industrial wastes in terms of oxygen that they will require if discharged into natural water courses in which aerobic conditions exist.

1.12 Nitrate - Nitrite

Analyses for nitrogen in its various forms have been performed on portable and polluted waters ever since man became convinced that water was a vehicle for the transmission of diseases. The present drinking water standards[5] lay down the upper limit of nitrate and nitrite Nitrogen of 45 mg/l as NO_3.[3,5]

Nitrate in water poses a greater health hazard but fortunately it seldom occurs in high concentrations. High nitrate level in water has been associated with development of methaemoglobinaemia in infants.[10, 11]

1.13 Fluoride

A fluoride concentration of approximately 1mg/l is an effective preventive of dental caries without harmful effects on health. Fluoride may occur naturally in water or may be added in controlled amounts. Some fluorosis may occur when fluoride level exceeds the recommended limits (Appendix B).

1.14 Metals in Water

Calcium and Magnesium

Both of them produce hardness in water. The effect of hard water on health has long been a subject of debate but there appears to be no cause to worry.[12] The amount of calcium even in hard waters is much less than the daily nutritional requirements, the human body needing approximately 0.7 - 1.09gof calcium per day, most of which must be secured from the food supply. In high concentrations magnesium salts have pronouced laxative effect.[13]

1.15 Sodium and Potassium

They occur in most natural waters. The level may vary from negligible to appreciable. The ratio of alkali bases i.e. of sodium and potassium to alkaline earth bases i.e. of calcium and magnesium is of particular significance in waters used for agriculture purposes and human pathology. Soil permeability has been found to be detrimentally affected by a high sodium ratio while certain diseases require water of low sodium concentrations. The percentage sodium can be expressed as

$$\% \text{ Na} = \frac{(\text{Na} + \text{k}) \times 100}{\text{Ca} + \text{Mg} + (\text{Na} + \text{k})}$$

Many factors including soil composition, structure etc of the irrigation ought to be taken into consideration. A 60% sodium content is considered the maximum permissible for agriculture.

1.16 Iron and Manganese

Iron is generally present in natural waters in concentrations less than 0.3 mg/l which is not of sanitary significance. However iron affects taste and odour and may stain fixtures due to formation of colloidal ferric hydroxide. Manganese is most generally present in natural waters in concentrations less than

0.05mg/l and has no toxicological significance.
Both of them however interfere with laundry operations and cause difficulties in distribution systems by supporting growths of iron bacteria.

1.17 Copper

Present only in small amounts in natural waters. Although some copper is considered essential to metabolism, it may stain porcelain at over 0.5 mg/l, it produces taste at 1 mg/l or more and seriously affect photographic process. The drinking water rejection limit is 1.0 mg/l which is also the aesthetic limit.[15]

1.18 Zinc

Zinc is an element essential in metabolism. It however produces a bitter astringent taste, threshold being reported all the way from 2 to 24 mg/l.
It can produce sandlike deposts in water supplies.
Zinc is needed for nutrition by most crops, but the amounts must be small since zinc concentrations of 0.3 to 10 mg/l have reportedly produced toxic symptoms in various plants grown in standard nutrient solutions.[4,5]

1.19 Chromium

The carcinogenic potential of hexavalent chromium is a good reason to protect a portable water supply against its intrusion. Chromium salts are used extensively in industrial processes especially in tanning and textile industries in the Northern part of this country, and the possibility of its entering the water supply through the discharge of waste cannot be ruled out. The standards lay down the limit of 0.05 mg/l Cr^{6+} (Appendix A).

1.20 Lead

The amount of lead in natural waters is usually low unless the gathering grounds are in the vicinity of some source of lead such as lead mines. Lead is dissolved by water from galvanized services. Lead is a toxic metal that tends to accumulate in the bones of man and animals. (Appendix A).

1.21 Aluminium

It is the third most abundant element of the earth's crust occurring in minerals, rocks and clays, hence its presence in practically all natural water supplies as a soluble salt a colloid or an insoluble compound. Soluble colloidal and insoluble aluminium

may appear traditionally in treated waters as a residual from alum coagulation. It has no sanitary significance.

1.22 Silica

Is present in most natural waters as poluble compound, larger concentrations of it are usually found in well waters derived from chalk soils. The presence of natural silica in river water is often an indication of the ability of the water to promote growth of certain organisms such as diatoms which require silica for their skeletal structure. It is added in certain treatment plant to assist the floc formation where coagulation is used.

1.23 Phosphates

These may enter surface and ground waters by leaching from mineral or ores in agricultural runoff, from industrial wastes. Water containing excessive phosphates may be desirable for use in food preparation because of a buffering action on the stomach acids.[5,8]

Limitations

Although no water can be certified as fit for drinking purposes until a detailed physical chemical and bacteriological analyses on it are carried out, the present study was confined to chemical examinations of raw and treated waters, natural waters from wells and industrial waste waters only.

It should however be noted that contamination is often intermittent and may not be revealed by chemical or bacteriological examination of a single sample. The examination of a single sample can only indicate no more than the conditions prevailing at the time of sampling. A satisfactory result cannot guarantee that the observed conditions will continue to exist in future.[3]

Results obtained from samples of industrial waste-waters and waterworks depend on the types of processes going on and the efficiency of the treatment processes prevailing at the sampling times.

CHAPTER 2

MATERIALS AND METHODS

(a) Sampling Procedure

Sampling is a most important part of the total process of water analysis. A water analyst ought to recognise the instability of the water sample and do his best to correct or prevent changes in the sample composition that may occur between the time of sampling and the time of analysis.

It is an axiom that the reliability of analytical results obtained in the Laboratory can never be more reliable than the sample upon which the tests are performed.

Some analytical results are in fact in error because of inadequate sampling procedure rather than because of faulty Laboratory techniques. With these guiding principles in mind, the author set about collecting the samples.

(b) Quantity of Sample

Each sample was collected in a 4 - litre polythene container with a screw cap and in a 3 x 250 ml. glass bottles with stoppers for dissolved oxygen determination (See Procedure for collection of samples for Dissolved oxygen determination).

(c) Time interval between collection and Analysis

It is known that generally the shorter the time that elapses between collection of a sample and commencement of its analysis the more reliable will be the analytical results, however, it is not possible to state unequivocably how much time may be allowed to elapse between collection of a sample of water and the analysis. It always depends upon the characteristics of the sample, the particular analyses to be made and the conditions of storage.

(d) Representative Samples

Care was exercised to obtain samples that were truly representative of existing conditions and to handle them in such manners that they did not deteriorate during transportation. The sample container was rinsed at least three times with the sample to be collected. Representative sample of industrial waste waters was obtained by making composites of samples which had been collected over a fairly long time and occasionally at different sampling points. Collection of sample was carried out on three different occasions on a particular water sample and sets of analyses were carried out on them.

Every sample collected was identified by a label on its container showing:-

(a) Nature of sample

(b) Time and date of collection

(c) location of sample

(d) P^H and temperature at the time of collection.

Samples from tap water and waterworks were collected only after the lines had been flushed for about five minutes to ensure that the samples were representative of the supplies.

(e) Field Analysis

For reasons outlined earlier on, certain analyses had to be carried out right at the spot. The following determinations were always made at the source of the sample:-

(a) Temperature

(b) P^H

(c) Residual Chlorine

(d) electrical conductivity

*(e) Dissolved oxygen

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*Was carried out on samples collected at Kaduna

Field kit was designed to contain the following

(a) Griffin portable P^H Meter type B17 DA

(b) Thermometer in ^oC

(c) Portable conductivity bridge type MC 3 EIL

(d) Three polythene bottles containing buffer solutions.

(e) Nessleriser discs.

Apparatus

All the pipettes and burettes, the 50ml, 100ml, 250ml and 1000ml flasks, the Nessleriser glass tubes were previously calibrated and they were found to be within reasonable tolerance limits. A 5ml microburette was used in the titrations and 1ml, 2ml, 5ml, 10ml and 50ml pipettes were used especially in alkalinity, chloride and hardness determinations.

(f) Standardisation of Methods and Preparation of Reagents

Though all the methods of analysis employed in this work are those of standard Methods[7] all of them had to be tried and standardised, and possibly modified. Because this type of work had never been done in the Department before so a lot of trials and standardisation had to be made to generate confidence in the results before starting the actual analysis hence it was

therefore not possible to analyse a wide range of samples within the time alloted to this work.

A lot of time was spent in preparing large number of reagents and only those that require special preparations and purifications will be mentioned in this work.

(g) Use of B.D.H. Lovibond Nessleriser

This is designed for sensitive colorimetric tests where it is necessary to look through a considerable depth of liquid to develop enough colour for accurate matching. The Nessleriser contains two hollow columns which enclose a pair of Nessler tubes placed above an opal glass reflector and below a rotating bakelite disc which holds the permanent glass colour standards. The Nessler tube containing distilled water or blank was placed in the left hand compartment and the coloured sample so produced in the test was placed in the right hand compartment. This disc was rotated until a match was obtained and the amount of substance present in the solution was recorded from the disc.

The Lovibond Comparator uses the same principle except that 10ml tubes were always used instead of 50ml. Nessler tube and the discs for Nessleriser are not interchangeable with those intended for comparator.[16]

Standardisation

Only the procedure for one particular standardisation and calibration will be described in this presentation. (See Tables XI and XII).

2.1 Determination of Residual chlorine[7,16,17]

Principle: The yellow colour produced on adding orthotolidine reagent to the water under test was matched with standard lovibond discs. Though the yellow colour is not specific for chlorine, being also formed by nitrites, determinations were restricted to treated water samples which are far less contaminated with nitrites.

Reagents.

Analar ortho-tolidine reagent was prepared by mixing

ortho-Tolidine (Analar)	1g
Hydrochloric acid (Analar)	100ml.
Distilled Water to produce	1000ml.

Procedure

To 50ml. of treated water sample in Nessleriser tube added 0.5 ml. of the ortho-tolidine reagent and the yellow colour developed was compared with distilled water (blank) using the appropriate standard chlorine disc. Results are as shown in Table I.

2.2 Determination of electrical conductivity

The portable conductivity bridge type MC.3 EIL was used in determining the electrical conductivity. The cell was rinsed with the sample and the sample poured into the cell unit until it was up to the top at edge of the bore. The temperature was measured with the thermometer. The selector switch was set to the appropriate range.X1, X10, X100 or X1000 the "ON" key depressed and the conductivity was recorded as shown in Table II.

Table I

Residual Chlorine determination

Samples	Residual chlorine (PPM)
1. Distilled water	less than 0.01
2. Treated Water ZWW*	0.5
3. Tap Water A.B.U.Z.+	0.09
4. Treated Water KWW*	0.5

* ZWW - Zaria Water Works

* KWW - Kaduna Water Works

+ ABUZ - Ahmadu Bello University, Zaria

Table II

Determination of electrical conductivity

Sample	Electrical Conductivity (umhos)	Temperature (^{o}C)
1. Distilled Water	1.80	24.5
2. Raw Water ZWW	0.30×10^2	24.8
3. Treated Water ZWW	1.0×10^2	24.9
4. Tap Water ABUZ	1.00×10^2	25.
5. Raw Water KWW	0.30×10^2	25.
6. Treated Water KWW	1.30×10^2	25.
7. Well 1	6.50×10^2	24.8
8. Well 2	6.70×10^2	24.7
9. Well 3	4.0×10^2	26.5^{o}
10. Industrial Waste-water FSPFC. KD	1.60×10^4	24.8
11. Industrial waste-water Nortex Nig. Limited	5.90×10^2	32.
12. Industrial waste-water, Kano Tanneries Limited	8.50×10^4	32.5

FSPFC: Federal Superphosphate and Fertilizers Company Kaduna.

2.3 Turbidity Measurement

Principle: A beam of light of standard intensity when passed through water sample is scattered by the suspended particles; the degree of light attenuation can then be related to turbidity.

Equipment

EEL nephelometer head

EEL Unigalvo type 200

Procedure:

The Unigalvo was installed as contained in the mannual.[18] The nephelometer head was connected to the input socket. The Unigalvo sensitivity control was adjusted to read 100 with the accompanied standard tube in its tube socket. The standard was replaced with a pyrex test tube containing 20 ml of distilled water and the metal cap was used to cover this. The instrument was adjusted to read zero. The standardisation was repeated three times and the distilled water was replaced with 20 ml of sample or suitable dilution of sample, and the scale reading was recorded. This represented the turbidity of the sample relative to the standards. The results are given in Table III.

Table III

Turbidity Measurements

Sample			Turbidity unit
1.	Distilled Water		0.
2.	Raw Water	ZWW	69.5
3.	Treated Water	ZWW	2.3
4.	Tap Water	ABUZ	2.3
5.	Raw water	KWW	87.5
6.	Treated water	KWW	5.80
7.	Well 1		2.30
8.	Well 2		2.30
9.	Well 3		3.00
10.	Industrial waste water FSPFC. KD.		88.0
11.	Industrial waste water. Nortex Nigeria Ltd.		92.00
12.	Industrial Waste water, Kano Tanneries Ltd.		500

2.4 Determination of Dissolved oxygen

The Winkler Method and its modifications are the standard procedures for determining dissolved oxygen.[7, 19] The determination depends upon the fact that oxygen oxidises $Mn^{(II)}$ to a higher valency state under alkaline conditions and that manganese in the higher valency state is capable of oxidising iodide to free iodine under acidic conditions. Thus the amount of free iodine released is equivalent to the dissolved oxygen originally present. The iodine is estimated by titrating it with standard sodium thio sulphate solution using starch as indicator.

The Azide Modification of the Winkler Method

The reactions involved are as follows:

$$Mn^{++} + 2OH^{-} \longrightarrow Mn(OH)_2 \downarrow \quad (1)$$

$$2\,Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2 \quad (2)$$

brown

$$MnO(OH)_2 + 2H_2SO_4 \longrightarrow Mn(SO_4)_2 + 3H_2O \quad (3)$$

$$Mn(SO_4)_2 + 2KI \longrightarrow MnSO_4 + K_2SO_4 + I_2 \quad (4)$$

The Azide Modification of the Winkler Method

This is the method used in the present study. It most effectively removes the interference caused by nitrite.

In acid medium nitrites react with potassium iodide liberating iodine.

$$2KI + H_2SO_4 \longrightarrow 2HI + K_2SO_4.$$

$$2\ HNO_2 + 2HI \longrightarrow 2H_2O + N_2O_2 + I_2.$$

If the sample is allowed to stand exposed to the air the oxygen which dissolved will react with N_2O_2 again to produce nitrite which will liberate more iodine. This will give higher results.

$$2N_2O_2 + 2H_2O + O_2 \longrightarrow 4HNO_2.$$

By using sodium azide in alkaline potassium iodide interference due to nitrite is overcome

$$2Na\ N_3 + H_2SO_4 \longrightarrow 2HN_3 + Na_2SO_4.$$

$$HNO_2 + HN_3 \longrightarrow N_2O + N_2 + H_2O.$$

Reagents

The following reagents were prepared

1. Standard 0.025N. sodium thiosulphate solution
2. Alkali - iodide azide reagent
3. Starch indicator [7,20].

Procedure

Collection of sample.

Samples were collected in 3 x 250ml separate bottles with glass covers. The samples were not allowed to remain in contact with air or agitated since either conditions could cause discharges in the gaseous content. In sampling from a line under pressure a rubber tube was attached to the tap and it extended to the bottom of the container and the container was allowed to overflow about five times its volume and the stopper replaced so that no air bubbles were entrained. Determination was made as soon as the sample arrived at the Laboratory or on the spot e.g. at Kaduna FSPC.

Special Flask used (203ml. standard flask)

Since a total of 4ml. (2ml. each) of the manganese sulphate and alkali iodide azide reagents were added to 250ml bottle containing the sample the volume taken for titration should be $\frac{200 \times 250}{250-4} = 203ml$?

A 200ml. standard volumetric flask previously calibrated was filled with distilled water to the mark and 3ml of distilled water was added with 5ml.

pipette and the flask was marked and was carefully cut at this mark, hence a 203 ml. standard flask was improvised.

To 250ml of sample, added 2ml of manganese sulphate solution,[7] followed by 2ml. of alkali-iodide reagent well below the surface of the sample. It was stoppered with care to exclude air bubbles and mixed by inverting the bottle several times. 2ml of concentrated sulphuric acid was added down the neck of the bottle. It was mixed by gentle inversion and 203ml. of the resulting solution was removed for titration using 0.025N sodium thiosulphate as titrant; and 1ml of starch as indicator.

Since 1ml. of 0.025N sodium thiosulphate titrant prepared is equivalent to 0.200 mg dissolved oxygen, each ml. of titrant used is equivalent to 1mg/l dissolved oxygen when a volume equal to 200ml of the original sample was titrated.

Results obtained are shown in Table IV.

Table IV

Results of Determination of Dissolved Oxygen

Sample	Dissolved oxygen mg/l
1. Raw water ZWW	7.0
2. Treated water ZWW	7.30
3. Tap water ABUZ	6.40
4. Raw water KWW	7.00
5. Treated water KWW	7.45
6. Well 1	2.50
7. Well 2	2.70
8. Well 3	0.70
9. Industrial waste water F.S.P.F.C. KD	1.10
10. Industrial waste water Nortex Nig. Limited. KD.	0.30
11. Industrial waste water Kano Tanneries Ltd.	0.20

2.5 Determination of Alkalinity

There are two standard methods for alkalinity determinations[7]

1. Potentiometric method for water samples of low alkalinity.

2. Indicator method

The indicator method is fairly rapid and found satisfactory for this particular work.

The determination was carried out by titrating 100ml of sample with 0.0201N H_2SO_4 to successive bicarbonate and carbonate equivalent points indicated by phenolphthalein and methyl orange respectively. About 0.1 ml (2 drops) of phenolphthalein indacator was added and sample titrated till the solution turned colourless and 0.1 ml. of methyl orange indicator added to the above solution and titration continued till a colour change from orange to pink was obtained.

The reactions taking place are as follows:

1. Hydroxide

$$2NaOH + H_2CO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

2. Normal Carbonate

$$2\ Na_2\ CO_3 + H_2SO_4 \longrightarrow 2NaH\ CO_3 + Na_2\ SO_4$$

$$2\ NaHCO_3 + H_2\ SO_4 \longrightarrow Na_2\ SO_4 + 2H_2CO_3$$

3. Bicarbonate

$$2\ NaHCO_3 + H_2SO_4 \longrightarrow Na_2\ SO_4 + 2H_2CO_3$$

The titration values were recorded in the work sheet and alkalinities were expressed as mg/l of $CaCO_3$

(a) Phenolphthalein alkalinity

$$\text{as mg/l } CaCO_3 = \frac{a \times N \times 50{,}000}{\text{ml of sample}}$$

(b) Total alkalinity (methyl orange)

$$\text{as mg/l } CaCO_3 = \frac{b \times N \times 50{,}000}{\text{ml of sample}}$$

where a = ml of titrant required to reach the end point with phenolphthalein

b = total titrant value to reach the second end point with methyl orange indicator.

The five possible alkalinity conditions in a sample of water are:

(a) Hydroxide

(b) Hydroxide and normal carbonate

(c) carbonate alone

(d) Normal carbonate and bicarbonate

(e) Bicarbonate.

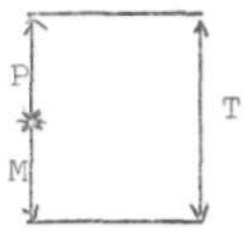


Table V

Showing alkalinity Relationships

Results of Titration	Hydroxide alkalinity as $CaCO_3$	Carbonate alkalinity as $CaCO_3$	Bicarbonate alkalinity as $CaCO_3$
1. P = T	T	0	0
2. P > ½T	2P-T	2(T-P)	0
3. P = ½T	0	2P	0
4. P < ½T	0	2P	T - 2P
5. P = 0	0	0	T

P represents alkalinity as shown by phenolphthalein

T = total alkalinity

M = T - P or the additional alkalinity shown by methyl orange beyond that shown by phenolphthalein.

This shows that:-

(a) Carbonate alkalinity is present when the phenolphthalein alkalinity is not zero but less than the total alkalinity.

(b) Hydroxide alkalinity is present if the phenolphthalein alkalinity is more than half the total alkalinity

(c) Bicarbonate alkalinity is present if the phenolphthalein alkalinity is less than half the total alkalinity.[7, 20]

Table VI

Results of Determination of alkalinity and P^H

Sample	P^H Value	Phenolphthalein alkalinity as mg/l $CaCO_3$	Total Alkalinity as mg/l $CaCO_3$
1. Distilled Water	5.6		
2. Raw water ZWW	6.4	0.	24.1
3. Treated Water ZWW	8.7	0.	27.0
4. Tap water ABUZ	8.1	1.0	25.1
5. Raw water KWW	7.6	0.	25.1
6. Treated water KWW	9.1	15.1	34.2
7. Well 1	5.5	0	26.1
8. Well 2	5.6	0	57.3
9. Well 3	7.0	0	187.9
10. Industrial wastewater FSPFC. KD	1.8	*0	0
11. Industrial wastewater Nortex Nig. Limited	10.6	0	197.0
12. Industrial wastewater Kano Tanneries	11.2	1,055	2,050.

* The acidity of FSPFC KD was determined to be 16,500 mg/l as $CaCO_3$.

2.6 Determination of Chlorides in Water

There are two similar methods for determination of chlorides in natural and industrial waste waters,[7] the argentometric method and the mercuric nitrate method. The argentometric method was used in the present study. This is based on differential precipitation of chloride and chromate ions, the latter serving as indicator to mark the end point by precipitating $Ag_2 CrO_4$ as brick red colour after all the AgCI has been precipitated provided the solution is neutral or slightly alkaline. $(Ag^+) \times (CI^-) \longrightarrow AgCI$

$Ksp = 1.2 \times 10^{-10}$

$(Ag^+)^2 \times (CrO_4^{2-}) \longrightarrow Ag_2 CrO_4 \quad Ksp = 1.7 \times 10^{-12}$

Sheen and Kahler[21] had shown that Mohr titration is unaffected by normal amounts of sulphates, alkalinity, hardness, phosphate silicate and iron.

Special Reagents

(1) Chloride free potassium chromate indicator

Dissolved 5g of pottassium chromate in distilled water and added silver nitrate solution dropwise until a definite red precipitate was formed. It was filtered after about twelve hours and filterate diluted to 100 ml. with distilled water.

(2) 0.0282N Silver Nitrate titrant

0.0282N silver nitrate solution was prepared and standardised against 0.0282N sodium chloride.

1ml of 0.0282N. $AgNO_3 \equiv$ 10ppm of chloride as Cl^- in 100ml of sample.

(3) Aluminium hydroxide suspension to remove interference[7]

(4) IN sodium hydroxide

(5) IN sulphuric acid

(6) 30% hydrogen peroxide

Procedure

To 100ml of sample (P^H between 7 to 8 adjusted with either sodium hydroxide or sulphuric acid) after determining total alkalinity, I added 1ml. of indicator and titrated the sample with standard 0.0282N. Silver nitrate solution until a permanent faint brick red colour was obtained.

A blank titration was also carried out and the chloride content of the sample was calculated as follows:

$$Cl^- \quad mg/l = \frac{(A-B) \times N \times 35,400}{ml \text{ of sample}}$$

or 1ml of 0.0282N. $AgNO_3 \equiv$ 10ppm of chloride as Cl^- in 100ml of sample. Results are given in Table VII

A = titration value for sample
B = titration value for blank
N = normality of titrant

Table VII

Results of Determination of chloride

Sample	Chloride as Cl^-, mg/l
1. Distilled water	2.0
2. Raw water ZWW	8.0
3. Treated water ZWW	8.0
4. Tap water ABUZ	5.0
5. Raw water KWW	7.5
6. Treated water KWW	8.0
7. Well 1	116.0
8. Well 2	103.5
9. Well 3	80.0
10. Industrial waste water FSPFC. KD	320.0
11. Industrial wastewater Nortex Nig. Ltd. KD.	37.0
12. Industrial wastewater Kano Tanneries Ltd.	184.0

ZWW	Zaria Water Works
ABUZ	Ahmadu Bello University Zaria
KWW	Kaduna Water Works
FSPFC	Federal Superphosphate Fertilizer Company
KD	Kaduna

2.7 Determination of Hardness

The accurate Method for determining hardness is to compute it from the results of complete mineral analysis. This method though considered to yield higher accuracy[7] was not used in the present study since a complete mineral analysis was not undertaken.

Blacher et al[20] recommended the use of standard solution of palmitate as a titrant for calcium and magnesium ions in neutral solution. When all the alkaline earth ions are precipitated, the solution becomes alkaline to phenolphthalein as a result of the hydrolysis of excess palmitate ion,

$$CH_3(CH_2)_{14}\ COO^- + H_2O \longrightarrow (CH_3)(CH_2)_{14}\,COOH + OH^-$$

The complexometric method using sodium salt of ethylenediamine tetra acetic acid disodium salt of EDTA was used as a titrant. EDTA and its sodium salt form soluble hexa dentate chelates with calcium and magnesium ions[23] releasing two moles of hydrogen ion for each mole of alkaline earth ion complexed.

When the indicator dye such as Eriochrome Black T. is added to metal ion solution, it also forms a complex with it but this is less stable than the

EDTA - Metal ion complex.[22]

Reagents

The following reagents were prepared:

1. 0.01M. disodium EDTA solution
2. Erio Chrome Black T. indicator
3. Buffer solution of P^H 10 [NH_4OH/NH_4Cl buffer]
4. Sodium hydroxide buffer.[7, 24]

To 100ml. of water sample 2ml. of ammonium chloride/ammonium hydroxide buffer was added followed by addition of 2 drops of indicator. The wine red solution was titrated with 0.01M EDTA, solution until the colour changed from wine red to blue at the end point.

M - Indicator + EDTA ——→ M - EDTA + Indicator
Wine red at P^H = 10 blue

Total hardness was calculated as follows:

$$\text{Total hardness} = \frac{a \times b \times 1000}{\text{ml. of sample}}$$

as mg/l $CaCO_3$

a = ml of titrant.

b = mg $CaCO_3$ equivalent to 1ml EDTA = 1 since 1 ml. of 0.01M EDTA [containing 3.7233g sodium salt of EDTA per litre as prepared above] = 1mg $CaCO_3$.

The results are given in (Table IX)

Determination of Calcium hardness

To 100ml of water sample added 2ml. of sodium hydroxide buffer; 0.4g of murexide indicator was added and the sample titrated with 0.01M EDTA solution until the colour changed from pink to purple. The calcium hardness was calculated as above. The difference between the total hardness and calcium hardness in mg/l $CaCO_3$ gave the hardness due to magnesium..

2ml of an inhibitor solution prepared from 4.5g hydroxylamine hydrochloride dissolved in 100ml of 95% ethanol was added to sample from Federal Superphosphate and Fertilizers Company, Kaduna to suppress interfering ions.

The results are given in Table IX.

The use of equivalent mg/l $CaCO_3$ as a unit for alkalinity and hardness facilitates the calculation of proper dosages in a number of operations in water treatmentand simplifies the comparison of analyses of different water supplies.

Table IX

Results of Determination of hardness

Sample	Calcium hardness as mg/l $CaCO_3$	Magnesium hardness as mg/l $CaCO_3$	Total Hardness as mg/l $CaCO_3$
1. Distilled Water	ND	ND	1
2. Raw Water ZWW	8.0	5	13
3. Treated Water ZWW	34.0	6	40
4. Tap Water ABUZ	36.0	4	40
5. Raw Water ZWW	8.5	5.5	14
6. Treated Water KWW	43.0	5	48
7. Well 1	85.0	51	136
8. Well 2	101.0	44	145
9. Well 3	123.	19	142
10. Industrial waste-water FSPFC KD.	5,900	1,100	7,000
11. Industrial waste-water, N.N. Ltd. KD.	48	10	58
12. Industrial waste-water Kano Tanneries	1830	130	1960

ND - Not determined.

2.8 Determination of Nitrate in water samples

The determination was based on the colour produced by the nitration of phenol - 2, 4 disulphonic acid. The following reagents were prepared

(a) Phenol - disulphonic acid 25% W/V[7]

(b) Ammonia solution A.R. 10% W/V.

Procedure

Took 5ml of 5 - fold dilution of the sample and evaporated to dryness in porcelain dish on boiling water bath 1ml of phenol disulphonic anid was added to the cooled residue, ensuring that the reagent was in contact with all the solid residue derived from the sample. It was allowed to stand for ten minutes. It was transferred to Nessleriser tube using 30 ml. of distilled water, cooled, and added 10 ml. of ammonia solution. It was cooled again and diluted to 50 ml. and the yellow colour was compared with Nessleriser Disc NHP previously calibrated. To eliminate chloride interference 1ml. of glacial acetic acid was added to 10ml. of sample followed by 0.1g of silver sulphate, shaking, and this was later filtered through whatman No. 42

filter paper. The above test was then applied to the filterate. The results are given in Table X.

* The markings on the disc represent the actual amount of nitrate Nitrogen(N) producing the colours in the test sample.[7, 17, 24].

Table X

Results of Determination of Nitrates in selected Water Samples

Sample	Nitrate Nitrogen (as N) %	Nitrate Nitrogen (as N) mg/l
1. Well 1	10	10
2. Well 2	2.5	2.5
3. Well 3	20	20
*4. Industrial waste-water, Nortex Nig. Limited Kaduna	25	50
5. Treated Water ZWW	below detection limit	below detection limit

* The dilution factor in samples 1 - 3 is 5 and for sample 4 is 10.

2.9 Determination of Phosphate[7,18,24]

Using Deniges Method (Modified)

The standard colour glass discs for phosphate determination are designed to match the blue colours produced by the reduction of phosphomolybdic acid with freshly prepared stannous chloride solution. The method is quite sensitive and is relatively free from interference by other substances.

Reagents

1. 10% ammonium molybdate added to a cooled mixture of 150 ml sulphuric acid (AR) and 150ml distilled water. This was stored away from light.
2. (a) 0.1g Pure tin
   (b) 2ml. hydrochloric acid (A.R)
   (c) 1 drop of 4% copper sulphate solution

The mixture 2 was warmed to dissolve tin, cooled and diluted to 10ml with distilled water. This was prepared just before commencement of determination.

Standardisation of Procedure and calibration of Phosphate disc 3/7.

Standard phosphate solution was prepared by dissolving 0.716g of dry potassium dihydrogen phosphate in 100ml./ of solution to obtain a solution containing

50 mg/l phosphate. The following solutions were prepared by dilution to 100 ml. with distilled water.

Table XI

ml. of stock solution	mg/l of PO_4^{2-}
4	2
8	4
16	8
32	16
40	20
44	22

10 ml. of each of standards was diluted to 45 ml. with distilled water, transferred into a Nessleriser tube and immersed in water bath at 25°C. Added 1 ml. of ammonium molybdate reagent, mixed thoroughly followed by addition of 0.2 ml. of stannous chloride reagent, mixed and diluted to 50 ml. with distilled water and immersed in distilled water for another five minutes. 10 ml. of resulting solution was compared in comparator, using disc No. 3/7 for phosphate and distilled water as the blank. A good match was obtained for all the standard colours in the disc except for the colour

corresponding to 20 mg/l where the colours were not quite matched after repeated trials. This was noted, and 10 ml of the sample was similarly treated using the calibrated disc No. 3/7.

Result obtained is given below.

Sample	Phosphate as P_2O_5 mg/l
Industrial waste water F.S.P.F.C. KD	30

2.10 Determination of Fluoride

It is possible to separate fluorides from other constituents present in water by distilling hydrofluoric acid from solution of the sample in an acid with higher boiling point. By using a large sample volume a quantitative fluoride recovery is approached and sulphate carry over is minimised by conducting the distillation over a broad temperature range.

Procedure

300 ml. of the sample from F.S.P.F.C. KD. was distilled in concentrated sulphuric acid/water mixture until the temperature reached 180°C.[7,24]. About 100 mg

of silver sulphate was added to the distilling flask. Analysis was performed on the distillate.

The Alizarin Visual comparison method which is sensitive to 0.05 mg/1 fluoride was used.[7]

Reagents

i. fluoride stock solution.

Dissolved 0.2210g anhydrous sodium fluoride in distilled water and diluted to 1 litre 1ml = 0.100mg F. 100 ml. of stock solution was diluted to 1000 ml. to produce 1 ml = 10ugF.

ii. Acid Zirconium alizarin solution[7]

Standard solutions containing 0, 1.0, 2.0, 3., 4, 6, 8, 10, 12, 15 ml of diluted fluoride solution were set up in 50 ml Nessler tubes, and diluted to the mark.

1ml. of distillate from sample was diluted to 50 ml. in Nessleriser tube. Added 5 ml zirconium Alizarin solution to each of the standards and sample, and were mixed thoroughly. The colour developed by the sample was compared with those of the standards [pink to yellow; after an hour] . A match was obtained between the colour developed by sample and the

Nessleriser tube containing 12 ml. of the diluted standard. The sample was pretreated to remove any residual chlorine by adding 1 drop of sodium arsenite solution.[7]

Calculation

$$mg/l\ F = \frac{A}{ml.\ of\ sample}$$

A = UgF determined visually

Sample	Fluoride as F^- mg/l
Industrial waste water FSPFC KD.	120

* The determination of phosphate and Fluoride was confined to sample from Federal Superphosphate and Fertilizer's Company, Kaduna.

2.11 Standardisation of Method of determining silica

Ammonium molybdate reacts with silica and any interferring phosphate present in water at an approximate P^H value of 1.2 to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid. The intensity of the yellow colour so produced is proportional to the silica concentration.[7,24]

Reagent:

1. 10% ammonium molybdate in water
2. 10% oxalic acid solution
3. 2N sulphuric acid

Calibration of Nesslerizer Disc NN. for silica

A set of artificial colour standards were made up using potassium chromate and borax solutions. The table below extracted from "Standard Methods"[7] was used in the preparation.

Table XII

Value in silica mg	ml of potassium chromate solution .63g/1	ml of Borax solution 10g/1	ml. of distilled water
0.00	0.00	25	30
0.10	1.00	25	29
0.20	2.00	25	28
0.40	4.00	25	26
0.50	5.00	25	25
1.00	10.00	25	20

Borax solution contained 10g of sodium borate decahydrate $Na_2 B_4O_7 10H_2O$ dissolved in distilled water and diluted to 1 litre.

The volumes of reagent in table XII were prepared and mixed and each was in turn placed in Nesslerizer tube and matched against 55 ml. of distilled water as blank in the left hand compartment of the Nessleriser using standard silica disc NN. There was a perfect match in the colours i.e. 0.1 mg. colour on NN Disc corresponded to 0.1 mg. of the standard solution prepared.

Treatment of the Sample

Two 50 ml. Nessleriser tubes previously calibrated were filled with the sample. One of them was treated as follows: 2ml of ammonium molybdate solution was added followed by addition of 4 ml of 2N H_2SO_4 and was mixed well. Exactly ten minutes later 1.5 ml of oxalic acid solution was added and again mixed and was placed in the right compartment of Nessleriser. It was matched against the untreated sample in the other column using Disc NN.

1 mg in 50 ml sample $\equiv$ 20 ppm (as SiO_2)

Samples containing higher silica concentrations were diluted appropriately.

Most colurless salts even when present in relatively large quantitites do not influence the colour produced in this test.

Results of Determination of Silica

Table XIII

Sample	Silica as S_iO_2 (ppm)
1. Distilled Water	2
2. Raw water ZWW	8
3. Treated water ZWW	12
4. Tap Water ABUZ	12
5. Raw Water KWW	8
6. Treated Water KWW	16
7. Well 1	40
8. Well 2	40
9. Well 3	50
10. Industrial wastewater F.S.P.F.C. KD	800
11. Industrial wastewater. Nortex Nig. Ltd. KD	60
12 Industrial wastewater Kano Tanneries	200

2.12 Determination of Metals in Natural and Waste Waters Using Atomic Absorption Spectrophotometer

The instrument functions on the principle resembling emission flame photometry since a sample is aspirated into flame and atomized. The major difference lies in the fact that flame photometry measures the amount of light emitted whereas in atomic absorption spectrosopy a light beam is directed through the flame into a monochromator and unto a detector that measures the amount of light absorbed.[27]

It is known that the vapour of an element which contains free atoms absorbs light having wavelength as that which the atoms of this element are capable of emitting. When light of this wavelength passes through a flame containing a cloud of free atoms of the respective element the intensity of the ray is diminished due to absorption. The measured decrease in the intensity of the light is proportional to the concentration of atom in the flame having a corresponding wavelength and hence, also to the concentration of the atoms in the solution. Light with correct wavelength range for different elements is provided by the use of appropriate lamp for each element.[28]

Equipment

Perkin Elmer Atomic Absorption Spectrophotometer, model 290 B.

Preparation of Standard Solutions

(1) Four standard solutions of concentrations 0.0, 0.1, 0.2, and 0.3 ppm. were prepared for determination of sodium.

(2) Four potassium standard solutions of concentrations 0.0, 1.0, 2.0, 3.0, were prepared. Lanthanum oxide solution was added to each of these solutions to make concentration of La 1% in the final solution

(3) Four standard calcium solutions of concentrations 0.0, 3.0, 6.0, 9.0 ppm. were prepared

(4) Five magnessium standard solutions of concentrations 0.0, 0.5, 1.0, 1.5 and 2.0 ppm were prepared.

Each of the calcium and magnesium standards contained 1500 Ug Sr/ml.

(5) Four zinc and copper standard solutions of conc 0.0, 0.5, 1.0, and 1.5 ppm. were prepared.

(6) Similar standard solutions were prepared for iron and chromium.[28]

Procedure

The standards were first fed into the instrument using the appropriate lamps and the samples were run. The amount of various elements was recorded directly from the instrument.

The results are given in Table XIV.

Table XIV

Results of Atomic Absorption Spectrophotometric Analysis

	Water Sample	Na ppm	K ppm	Ca ppm	Mg ppm	Fe ppm	Zn ppm	Cu ppm	Cr ppm	Co ppm
1.	Distilled Water	--	--	--	--	--	--	--	--	--
2.	Raw Water ZWW	5.0	3.0	3.50	1.40	2.77	0.01	0.01	0.	0.
3.	Treated Water ZWW	5.50	2.50	14.10	1.30	0.	0.	0.02	0.	0.
4.	Tap Water ABUZ	4.50	2.90	15.30	1.30	0.	0.	0.02	0.	0.
5.	Raw Water KWW	5.50	2.70	3.80	1.70	2.64	0.03	0.	0.	0.
6.	Treated Water KWW	5.25	2.50	17.80	1.50	0	0.	0.	0.	0.
7.	Well 1	72.5	8.	34.10	12.90	0.12	0.02	0.	0.	0.
8.	Well 2	67.5	10.6	40.6	10.5	0	0.02	0	0	0
9.	Well 3	35	8	52.4	3	0	0.05	0	0	0
10.	Industrial Waste-Water FSPFC	625	12.10	2,400	280	45.5	1.34	0.40	0.54	0.37
11.	Industrial Waste-Water Nortex Nig.	900	45.2	19.5	2.40	0.47	0.04	0.03	0.14	0.03
12.	Kano Tanneries	900	105	760	5.90	0.85	0.26	0.04	10.25	0.07

2.13 Spectrophotometric Determination of Manganese in Water

Small amount of manganese can be determined rapidly and accurately by oxidation to permanganic acid and comparison with those of the standards treated in the same way. The best oxidant for the colorimetric determination is potessium periodate proposed by Willard and Greathouse.[29]

The reaction is as follows:

$2\ MnSO_4 + 5\ KIO_4 + 3H_2O \longrightarrow 2HMnO_4 + 5KIO_3 + 2\ H_2SO_4$. In the presence of excess periodate the colour is stable and Beer's law is obeyed over a wide range. Reducing agents interfere and can be removed by fuming with nitric acid - sulphuric acid mixture, and interference due to iron is prevented by addition of phosphoric acid.

Preparation of Standards

0.150g of high purity manganese metal [99.95%] was dissolved in dilute nitric acid, was boiled cooled and diluted to 1 litre with distilled water.

Treatment to produce colour

1, 2, 3, 4, 5, 6, 8 and 10 ml. of the standard solutions were transferred to 250 ml. conical flasks, diluted to about 50 ml with distilled water. 20 ml of concentrated nitric acid was added to each followed by 15 ml. of syrupy phosphoric acid and about 1g of potassium periodate was added to each flask and was heated to boiling. This was boiled for one minute and cooled. Each was transferred quantitatively into 100 ml standard flask and made up to mark with distilled water. The absorbance was measured at 535 nm against a blank.

50 ml. of each of sample solution was similarly treated and the absorbance values recorded. The concentration of manganese in the samples was calculated from calibration curve Table XV. The results are given in Table XVI.

Table XV

Spectrophotometric Determination of Manganese in Water

Calibration Curve.

ml of stock solution	Concentration [mg/l]	Absorbance
0.5	0.75	0.035
1.0	1.50	0.080
2.0	3.0	0.135
3.0	4.5	0.21
4.0	6.0	0.27
5.0	7.5	0.35
6.0	9.0	0.40
8.0	12.0	0.53

A graph of Absorbance against concentration was plotted. See Fig. 2.01.

Table XVI

Results of Determination of Manganese

Sample	Concentration mg/l	Absorbance
1. Well 1	1.44	0.065
2. Well 2	1.44	0.065
3. F.S.P.F.C.	2.80	0.125
4. Well 3	1.56	0.070

Spectrophotometric determination of manganese in vate

Graph showing the plot of Absorbance against Concentration.

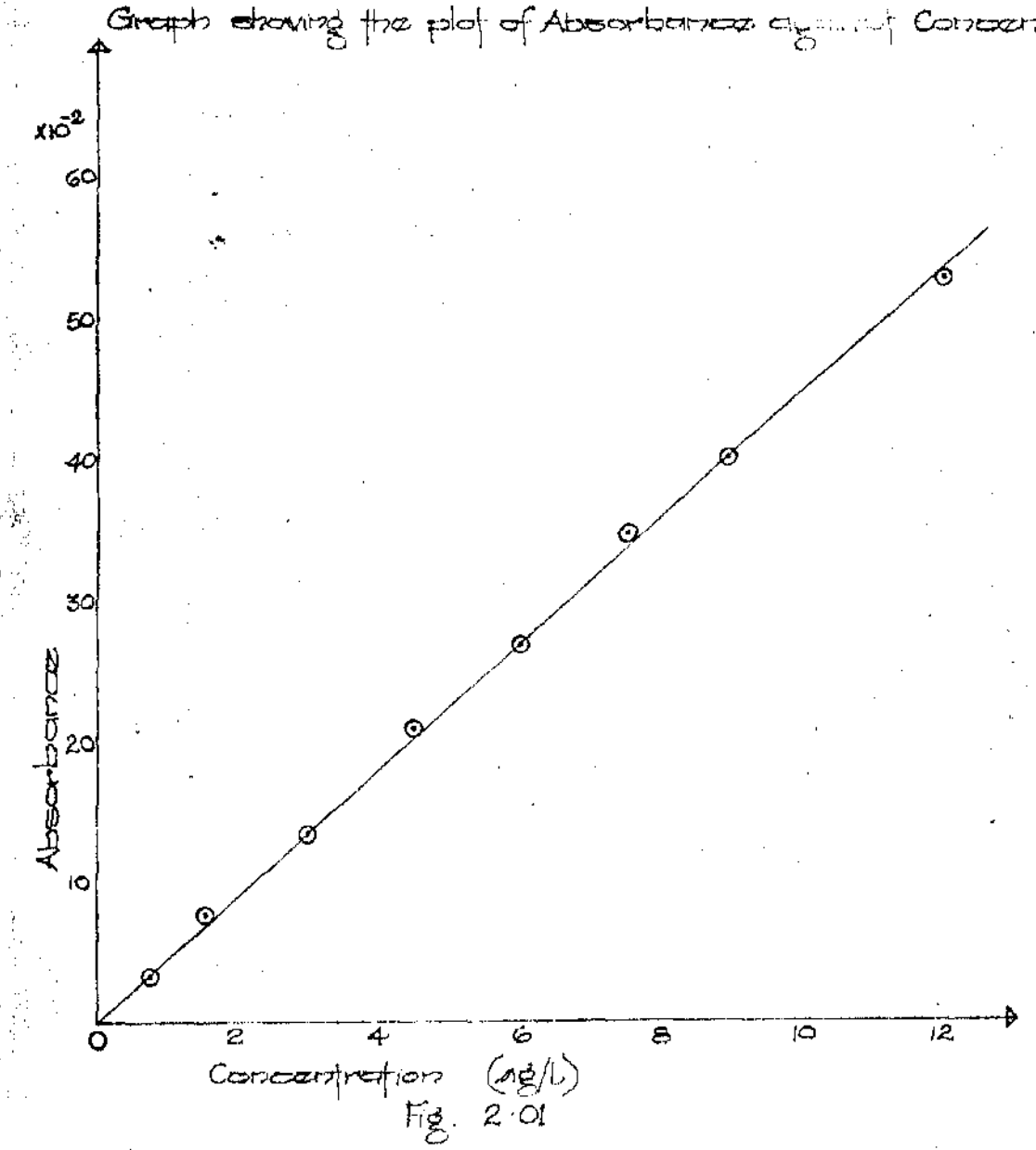


Fig. 2·01

2.14 Determination of Aluminium

Aluminium can be determined as oxinate and extracted quantitatively at P^H value of 4.5 to 5.0 [acetic acid buffer]. Thus it can be separated from a number of interfering elements including Be(II), Th (IV) etc. More specific separation can be obtained by operating in an ammoniacal medium at P^H value of 9 in the presence of tartarate, cyanide and hydrogen peroxide.

Reagents

The following reagents were prepared:

(a) oxine solution containing 2g of oxine dissolved in 100 ml of chloroform.

(b) Potassium cyanide, 13% in water.

(c) sodium sulphite, 20% in water

(d) Tartaric acid, 10% in water

(e) Hydrogen peroxide 10 volume

Standard solution of Aluminium

0.5013g of 99.9% Alluminium was accurately weighed, dissolved in hydrochloric acid and was made up to 500 ml with distilled water. The strength of the solution was 1.0026 g/l.

Procedure

Preparation of Calibration curve

0.05 ml, 0.1, 0.15, 0.2, and 0.30 ml of the stock solution was pipetted using micropipette into each of five beakers. 2ml of tartaric acid and 1 ml of hyrogen peroxide were added. They were allowed to stand for five minutes and 5 ml of sulphite solution was added. After standing for a further three minutes 10 ml. of cyanide solution was added and the solution was heated to 70°C and later cooled to 25°C. 2g of ammonium nitrate was finally added and the P^H adjusted to 9 with ammonia or HCl. The solution was transferred into a separating funnel. 5 ml. of oxine was added and the funnel was shaken for two minutes. The solution was allowed to settle and the organic phase was collected in 50 ml volumetric flask. This extraction was repeated three times, the solution was made up to 50 ml with chloroform. The absorbance was determined at 389 nm in comparison with a blank.[30]

The Results are given in Table XVII.

Table XVII

Determination of Aluminium in Treated Waters

Spectrophotometric Method

Calibration Curve

A graph of Absorbance against concentration was plotted see Fig. 2.02.

Concentration mg/ml.	Absorbance
0.05013	0.170
0.10026	0.32
0.15039	0.53
0.20052	0.72
ZWW	0.29
KWW	0.23

Smaples Readings

Kaduna Water Works Treated Water 0.23 (a)

Zaria Water Works 0.29 (b)

Corresponding Concentrations are (a) 0.066 mg.

(b) 0.083 mg.

Using 200 ml of the sample each

200 ml of sample contained 0.066 mg. Al

∴ 1000ml of sample " $\frac{0.066 \times 1000}{200}$

$= .33 mgl^{-1}$ Al.

Similarly for sample 2 $= 0.415 mgl^{-1}$ Al.

Spectrophotometric Determination of Aluminium in treated water sample

Graph showing the plot of Absorbance against Concentration

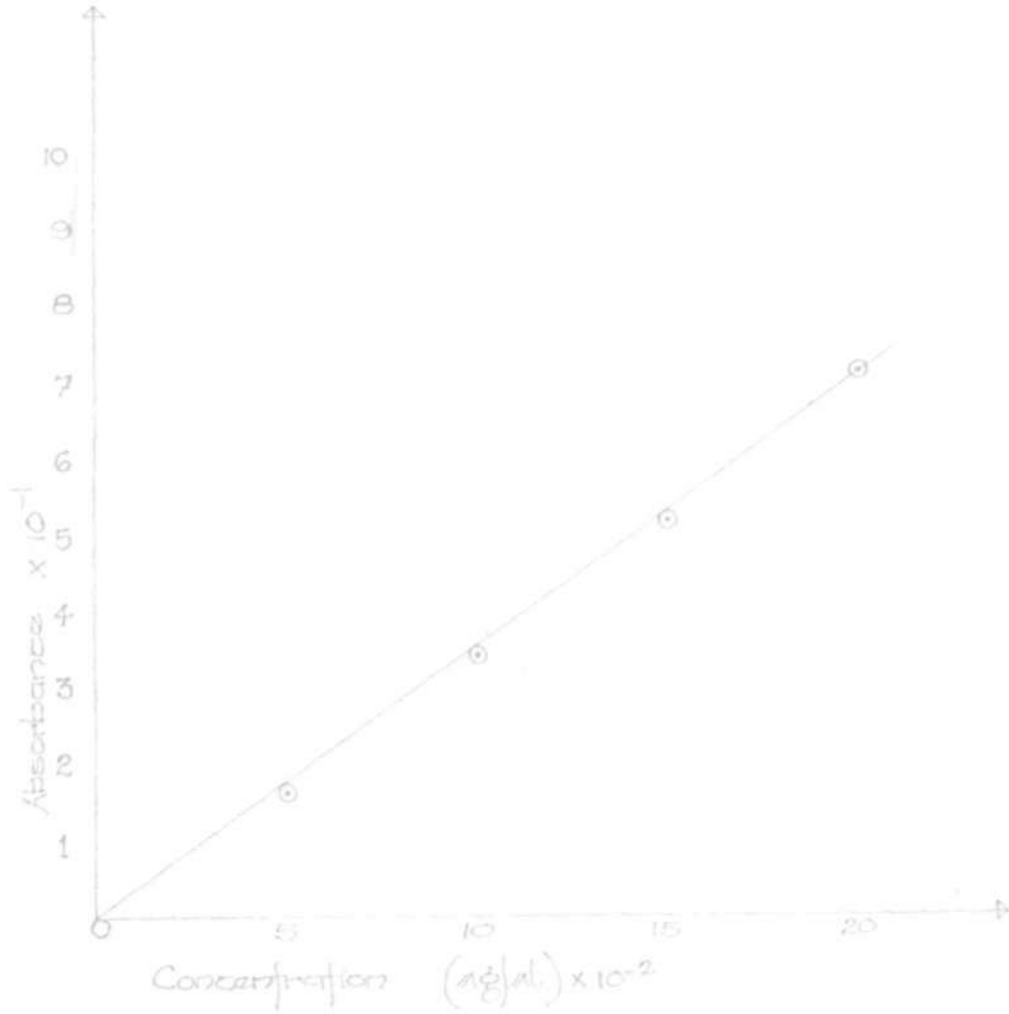


Fig. 2·02

Table XVIII

Comparison of data of Atomic Absorption Spectrophotometric analysis and EDTA titration

Sample	Ca (ppm) by Atomic Absorption Spectrophotometer	Ca (ppm) calculated from EDTA Titration
1. *Distilled Water	-	-
2. Raw Water ZWW	3.50	3.20
3. Treated Water ZWW	14.10	13.60
4. Tap Water ABUZ	15.30	14.40
5. Raw Water KWW	3.80	3.40
6. Treated Water KWW	17.80	17.20
7. Well 1	34.10	34.00
8. Well 2	40.60	40.40
9. Federal Superphosphate	2,400	2,360
10. Nortex Nig. Ltd.	19.50	19.20
11. Kano Tanneries	760	732
12. Well 3	52.40	49.20

* Blank.

3.1 Table XVII shows values of calcium obtained from Atomic Absorption Spectrophotometric analysis and values determined by EDTA titration methods. [See also Table IX]. The values from EDTA titrations are slightly lower than those from AAS analysis. The slight differences in values may be due to the author's error in estimating accurately the end points in titrations, his techniques of pipetting solutions, errors in apparatus even though they were previously calibrated and interferring ions that may be present in sample which can obscure the end points. In spite of all the above the author believes that there are good agreements between the set of values in the two columns to instil enough confidence in my results. This was one of the attempts made to standardise the reagent and method employed in this study.

3.2 Discussion

Raw and Treated Water Samples

(i) Residual chlorine determination

Results presented in table I represent the average values obtained from analyses carried on the samples over a period of three months.

The information was collected from the treatment sections of Zaria and Kaduna water works that 1 ppm of chlorine is constantly being added as a disinfectant to water supplied to the consumers. Experimental results (Table 1) show that half of this value 0.5 ppm of residual chlorine could be detected even in samples obtained and tested right at the water works. 0.09 ppm of residual chlorine was obtained on analysis carried out on tap water at Ahmadu Bello University, a distance of about 20 km. away from the treatment plant. In fact there are variations in the values obtained, because as low as 0.02 ppm of residual chlorine was detected in the course of this study.

The results, therefore, indicate that not all the chlorine dosed into the water got to the consumers. Of course chlorine is a gas, and is difficult to be retained in water. We can explain this in terms of the fact that ammonium sulphate is also being added to the water in the treatment process. This is to hold back the chlorine in water. This leads to the formation of chloramines. Chloramines are less oxidising and germicidal agents than chlorine but they are more stable and hence an active residual

form remains in water for a much longer period (several days) in the treated water.[4]

The reaction which takes place between chlorine and ammonia can be represented as follows:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$$

$$NH_3 + 2HOCl \longrightarrow NHCl_2 + H_2O$$

$$NH_3 + 3HOCl \longrightarrow NCl_3 + H_2O \qquad (4,6)$$

The formation of chloramines (mono, di and tri chloramines) depends on the P^H and relative amounts of each present. Ammonia - chlorine treatment can often be of tremendous advantage especially in Kaduna and Zaria water works, where water supplied to the consumers are retained in big tank reservoirs and mains for sometimes before delivery to the consumers This type of treatment is beneficial for controlling bacterial growth in long pipes and suppressing the development of iron fixing and slime forming types of bacterial growth. The concentrations of ammonia and chlorine are maintained always at 1:4 ratio.

(ii) P^H value alkalinity and Hardness

Table VI shows the results obtained for P^H values, and alkalinity determinations. P^H values of water samples have increased from 6.4, 7.6 for raw waters [Zaria water works, and Kaduna water works] to 8.7 and 9.1 for treated water respectively. Experimental results from table VI also show that total alkalinity for treated water is greater than that of the raw water from which it is derived. The treated water samples have now become much harder than the raw water obtained from the river water. The explanations for this lie in the fact that in the treatment process at the waterworks, Aluminium sulphate which is the most commonly used coagulant is being added and this increases the acidity of the water. Black[31] has discussed the mechanism of coagulation by aluminium salts and also the use of starch gelatine and synthetic polylelectrolytes as aids in coagulation. In order to raise the P^H and alkalinity of the treated water lime is normally added in the preliming and post liming treatment processes. This also reduces the possible corrosive action of water on metals and

and the water consequently becomes harder. Addition of lime also reduces the possibility of dissolution of heavy metals.[4] The P^H of domestic water supplies should lie within 6.5 to 9.0. Outside this range water may acquire a sour taste and corrosive to hot water services. Treatment processes, especially coagulation are affected by the P^H at which they are carried out, where necessary raw water P^H will need to be adjusted to give optimum coagulation. The values obtained here for P^H, alkalinity and hardness are within the WHO international standards recommended [See Appendix C].

Calcium is an essential mineral element for bone formation, some of which may be obtained through drinking water. Water for domestic use containing alkalinity in the range of 30 - 500 mg/1 as $CaCO_3$ is generally acceptable[5]. However excessive alkalinity can cause gastro-intestinal irritation. Besides, problems in treatment and distribution systems can occur when alkalinity is greater than the recommended values. [WHO standards].

Experimental results [Table IX] show that the magnessium hardness remains almost constant in both raw and treated waters. This is not unexpected since only calcium from lime is added to the raw water in the treatment process. Calcium hardness has gone up from 8 and 8.5 to 34 and 43 for raw and treated waters, respectively. These values have been confirmed by the results obtained from Atomic Absorption Spectrophotometric analysis for metals [Table XIV] The electrical conductivity has increased [Table II] showing that the total number of conducting ions has increased as a result of treatment.

(iii) Silica Determination

On examining Table XIII, the following inference can be drawn. The treated water has been polluted with silica. There are now more silica in the treated water than the raw water from which it is obtained. The additional silica from the treated water over that of the raw water can only come from the sand baths in the filteration process, although no health risks is anticipated in having this much silica in our drinking water supplies.

(iv) Other Metals in drinking Water

Because aluminium sulphate is used as a coagulant in treatment process of water in Zaria and Kaduna water works, I decided to investigate how much of aluminium is present in drinking water. Some soluble forms of aluminium may at times pass through filters into the water supplies. Results obtained [Table XVII page 66] show that 0.33 mg/l Al and 0.42 mg/l Al were obtained in Kaduna and Zaria waters respectively. These concentrations of aluminium in public water supplies are not problems of any sanitary significance. Even the use of Aluminium cooking utensils and baking powder containing aluminium has been shown to give no evidence of toxicity or other adverse effects.[32] It is interesting to observe that the treated waters become far less turbid than the raw water [Table III], even though some mineral elements have been added.

3.3 Well Waters

The well waters generally contain low dissolved oxygen as shown in [Table IV]. The low values obtained may be explained by the fact that many chemical and biochemical activities may be going on thereby consuming

the dissolved oxygen. Values obtained are below the 5 mg/l minimum value prescribed by WHO Standards [Appendix C]

In most instances involving the control of well pollution it may be desirable to maintain conditions favourable for the growth and reproduction of fish and aquatic organisms. Well 3 which is situated in the University main Campus Zaria, always remains closed and it is not normally used except in periods of emergency and acute shortage of water in the University when it is used for washing and cooking.

The nitrate levels in the wells are quite considerable [Table X] especially in well 3 which compares with the maximum permissible value recommended by WHO [Appendix B]

The illness of infantile methaemoglobinaemia[11,33] is not expected because infants adults inclusive in the university do not drink the water from this well; but wells 1 and 2 are the usual sources of water supplies to many people in Samaru village.

The silica content of the wells are generally much higher than the values obtained for treated waters and raw waters [Table XII] This may be attributed to the geological formation of the soil through which the well water has percolated. Only one of the wells contains 0.12 mg/1 of iron which is about the maximum value recommended by the WHO standards.

The high calcium magnesium and chloride contents [Tables VII and XIV] can be explained in terms of the geological formation of the Samaru soil which is likely to contain a lot of these elements.[34, 35.]

Atomic Absorption Spectrophotometric analysis revealed the presence of trace concentations of zinc in the wells. I believe no health risk is being run in taking this much zinc in the wells waters.

The dissolved oxygen concentation in the wells is dependent on the relative rates of biochemical depletion and reaeration. It is almost certain that biochemical depletion of oxygen occur in all these wells when the organic matter or free ammonia is oxidised by bacteria and micro-organisms.[5]

Spectrophotometric determination of manganese (Tables XV and XVI) shows appreciable amount of manganese in Samaru wells. This had been reported by Dr. J.A. Ogunrombi.[36] The values obtained in this work exceed the WHO recommended values of 0.1 mg/l in normal drinking water. No harmful physiological effects have been reported to follow the use of water containing concentrations of manganese encountered.

3.4 INDUSTRIAL WASTERS

(a) Federal Superphosphate and Fertilizer Company Kaduna

This is a chemical industry where sulphuric acid and superphosphate are produced side by side. The raw materials used are elemental sulphur and phosphate rocks. The phosphate rock is a complex of calcium, phosphate and fluoride (apartite) and it is accidulated with sulphuric acid to release the phosphate in slurry form. This stays for about 10 - 15 days and later cured at room temperature or at about 40°C, and later broken into granules and dried.

The byproducts are hydrogen fluoride, HF, and gypsum, $CaSO_4 \cdot 2H_2O$.

Personal investigation revealed that the wastewater is discharged untreated into river Kaduna. The high acid content P^H value of 1.8 and the acidity of 16,500 mg/l determined as $CaCO_3$ should be of great concern to the people. [Table VI.] Toxic chemicals such as chromium are also being discharged in significant quantities.

As much as 120 mg/l of fluoride is being discharged in to river Kaduna by this industry alone [as already determined.] Although a low concentration of fluoride in drinking water [0.6 - 1.7 mg/l depending on the average maximum daily air temperature] is desirable for young children. Fluoride has been shown to lower the incidence of dental caries.[2,5] However, higher levels of fluoride may cause dental or skeletal fluorosis in some individuals and excessive levels could be quite harmful. At present not much danger is anticipated as a result of this discharge because the amount is relatively small compared with the volume of river water hence this is constantly being diluted. In the nearest future

it is envisaged that as more and more is discharged it may accumulate in the river basin and may eventually pollute the river.

Chromium concentration of 0.54 ppm constantly discharged from the industry can serve as a source of future pollution to the river also; however the toxicity of chromium salts towards aquatic life varies with the organisms living in the river, temperature, P^H, valence of the chromium, and synergistic or antagonistic effects.[5]

(b) NORTEX NIGERIAN LIMITED

The results obtained here should be of great importance to the health inspectors in Kaduna because there are over six textile industries in Kaduna that discharge their effluents either directly or indirectly into river Kaduna. The processes involved here are bleaching and dyeing of cotton yearn or fabric. The most polluting waste water is from boiling of goods with alkaline solution e.g. sodium hydroxide or sodium carbonate. Toxic chromium, zinc and copper were found to be in trace amounts and it is hoped that they are being diluted as they discharge into the main river Kaduna. The use of sodium silicate

in scouring process explains the high silica content in the wastewater.

(c) KANO HOLTS NIGERIAN TANNERIES

Tanning process is one in which the putrescible proteins in animal skins are preserved. The process in Kano consists of soaking the hides and skin in tropical chloride of lime (TCL) to remove fats and flesh left after flaying. These are later put in drums to remove excess alkalinity since they cannot be tanned with alkalis. The skins are later scudded to remove the inter fibre hair.

The industrial effluent obtained from this place like the other two industries was not treated before being discharged. However the wastewater here was not being discharged into any stream, either because the industry is in an isolated place, a-way from any other industry or because there is no big river, where it can discharge. It is anticipated that when this industry becomes connected with other industries in Kano it may likely be discharging the wastewaters into the main sewer. Right now Kano Tanneries discharges effluents untreated, into a pit about five kilometres from Kano metropolitan

town. Any toxic or harmful chemicals detected as a result of this analysis cannot therefore constitute health risk to consumer of drinking water in Kano.

However, the possible soil pollution and the harmful effects of the chemicals on plants in the environment where these waste waters are being discharged cannot be overlooked.

Experimental findings [Table XIV] revealed that 10.25 ppm of chromium was being discharged constantly. A large number of workers[5] have found chromium as both chromic and chromate ions to be toxic to plants. Tolerance, however varies with plant species, the more sensitive plants being adversely affected in nutrient solutions containing 5 mg/l of chromium.[37] Turner and Rush 1971[38] found that chromium concentrations as low as 0.5 mg/l in water cultures or 10 mg/kg in soil cultures signigicantly reduced the yields of two varieties of soybeans.[39, 40] The consoling assumption is that the wastewater is not being used for irrigation pruposes in Kano and around. But the local farmers should be educated and discouraged from using the dumped waste waters as fertilisers.

The extremely low dissoved oxygen 0.2 mg/l [Table IV] is not unexpected and this shows that there are a lot of organic matter consuming the oxygen and because of high temperature 32°C at the point of discharge. Other toxic metals such as Zinc and copper are only present in insignificant concentrations.

The Federal Government ought to take step to regulate and supervise the trade effluents being discharged by various manufacturing industries in this country. (See Appendix D).

Conclusion:

Some of the experimental procedures employed in this study e.g. determination of nitrates, phosphate and fluoride, depend upon matching of colours by eye. In spite of the fact that the apparatus and discs have been previously calibrated and the author had series of trials in getting used to the technique, the limitations of these procedures should be noted. Colorimetric methods both visual and photometric methods are extremely very sensitive and

have been accorded prominent place in water analysis. The accuracy of the visual colorimetric method should always be evaluated in order to obtain reliable results. The tall form Nessler tubes provide a 30cm light path and this is desirable especially when faint colours are to be compared. The Nessleriser, the tubes, and discs, are inexpensive, portable and their use does not need much training, they are neither subjected to mechanical or electrical failures. They are however subject to personal bias, depending upon the analyst eyesight and cannot be claimed to have superior accuracy. On the whole they have been used and found suitable for routine analysis.

The author recommends that the water authority should be encouraged to carry out short chemical examinations of water at least once a month and complete chemical and bacteriological examinations of water once every three months.

Analysis of water coming from tap at Ahmadu Bello University gave insight into the quality of treatment given to drinking water in Zaria. From tables of result one can compare the analyses before and after treatment process. The analyses indicate

that the overall system is acceptable water treatment process since some impurities are removed. For example (Table III) shows that the turbidity has been almost completely eliminated although some mineral elements have been added as revealed by the electrical conductivity and hardness determination. On the whole the quality of our water seems to meet the WHO international standards. It is to the credit of the water supplies authority that poisonous chemicals like lead, and arsenic were not detected throughout the period of analysis.

In view of the many advances in techniques technical and medical information and in view of the importance of water to the public for drinking, irrigation and industrial purposes the author suggests that the Federal Government of Nigeria should establish Standards of Water Quality through the Government Chemistry Division, because a standard by which to judge the quality of our water is a necessity.

The WHO report of 1961 in Standards for Drinking Water gave the list of certain chemical substances which if present in supplies of drinking water at above certain levels of concentration are likely to give rise to actual danger to health. This is shown below.

APPENDIX A

TABLE A : LIMITS OF TOLERANCE FOR TOXIC SUBSTANCE IN PIPED SUPPLIES

Substance	Upper Limit of concentration
1. Lead as Pb	0.1 mg/l or about 0.001m . eq../l
2. Arsenic as (As)	0.2 mg/l or about 0.008 m eq./l
3. Selenium as Se	0.05mg/l or about 0.0013 m. eq/l
4. Chromium as Cr. hexavalent	0.05mg/l or about 0.006m eq/l
5. Cadium as Cd.	0.05 mg/l or about 0.0009m. eq/l
6. Cyanide as CN	0.01 mg/l or about 0.0004m. eq/l
* 7. Radioactivity	It is important to keep the radioactivity of drinking water as low as possible. The following are acceptable as upper limits in drinking water for lifetime use for large populations: alpha - emitters: 1 pico-curie / litre beta emitters: 10 pico-curies / litre

* My study did not include radiochemical analysis of water.

The presence of any of these substances in excess of the concentrations quoted should constitute grounds for the rejection of the water for use as piped supply.

* 0.1 mg/l of lead (as Pb) has been recommended as the upper limit in the supply but in certain undertakings where lead is still being used in piping the concentration of lead in water after prolonged contact with the pipes could be higher; but in instance should the concentration of lead as (Pb) exceed 0.3 mg/l after 16 hours contact with the pipes. However if the limit of 0.3mg/l is regularly exceeded it will be necessary to take steps either to change the piping or treat the water.

APPENDIX B

Harmful Constituents in Water

Constituents in water which if present in excessive amounts may give rise to trouble.

Substance	Nature of trouble which may arise	Approximate level above which trouble may arise
1. Fluoride as F	Fluorosis	1.5mg/l or about 0.079m.eq/l.
2. Nitrate as No_3	Danger of Infantile methaemoglobinaemia if water is consumed by infants.	50mg/l or about 806m. eq/litre
3. Copper as Cu.	Astringent taste; discoloration and corrosion of pipes, fittings and utensils.	0.05mg/l or about 0.0016m. eq/l at pumping station. 3.0mg/l or about 0.094m. eq/litre after 16 hours contact with new pipes.
4. Iron [total as Fe]	Taste, discoloration; deposits and growth of iron bacteria, turbidity.	0.1mg/litre, or abut 0.0036m. eq/l as the water enters the distribution system
5. Manganese as (Mn)	Taste; discoloration deposits in pipes; turbidity.	0.1mg/l or about 0.0036m eq/litre
6. Zinc as Zn	Astringent taste opalescence and sandlike deposit.	5.0mg/litre or about 0.153m eq/litre.
7. Magnesium as (Mg)	Hardness, taste	Not more than 30mg/ litre or about 2.47m eq/litre if there are 250mg/l orabout 5.2m.eq/l of sulphate; if there is less sulphate, magnesium up to125mg/l or about 10.28 m. eq./litre may be allowed.

APPENDIX B (Cont'd)

Substance	Nature of trouble which may arise	Approximate level abo e which trouble may arise
8. Sulphate as SO_4^{2-}	Gastro-intestinal irritation	250mg/litre or about 5.2 m. eq/l
9. Chloride as Cl	Taste, corrosion in hot water system	350mg/l. or about 9.87 m.eq/l. This limit may be exceeded in certain existing conditions which hygiene authorities will determine
10. Phenolic compounds as Phenol	Taste; particularly in chlorinated water	0.001 mg/l.

* It is advisable that if any of the above substances is present in piped supply at higher concentations than those given in the table, steps should be taken to adjust the concentrations.

APPENDIX C

This table contains a list of substances whose level should preferably be controlled.

Substance	Nature of trouble which may arise	Approximate level above which trouble may arise
1. Ammonia as NH_4^+	Growth of organisms Danger of corrosion in pipes. Difficulties in chlorination	Not more than 0.5mg/l. or about 0.028m. eq/l.
2. Free Carbon dioxide	Damage to pipes Danger of bringing metals into solution	For aggressive carbon dioxide - zero. This analysis should preferably be carried out at the time of collection of the sample.
3. Dissolved Oxygen	Taste and odour. Corrosion, Growth of organisms. If the conc. of dissolved oxygen is less than 5mg/l.the formation of protecting layer will be hampered thus causing all the free carbonic acid of non aggressive water to be corrosive to iron piping.	Preferably at least 5 mg/l. A special sample is required for this test.
4. Total hardness	Excessive scale formation. Danger of dissolving heavy metals if the level of hardness is below the recommended limit.	Limits of hardness 2-10m eq/l. 100-500 mg/l $CaCO_3$

* The levels for all substances in this table, with the exception of dissolved oxygen are thosewhich it is preferable not to exceed. For dissolved oxygen the concentration should preferably be kept above the level given.

APPENDIX D

Standards for Trade Wastes

Trade effluents to be discharged into rivers or streams should not include any of the following substances in proportion greater than those stated below.[41]

1.	P^H	6 to 9
2.	Suspended solid	30ppm
3.	Suspended and dissolved metals	30ppm
4.	Alkalinity as $CaCO_3$ (mg/l)	50ppm
5.	Free chlorine. Not more than	1.0ppm
6.	Sulphides as H_2S	1.0ppm
7.	Permanganate value at 27°C	60ppm
8.	Cyanides as HCN	0.2ppm.
9.	Temperature	110°F
10.	Oil, grease, fat not more than	10ppm
11.	B.O.D. at 20°C for 5 days	20ppm
12.	Phenols	1.0ppm
13.	Radioactive substance. There should be none	
14.	Arsenic, Copper, Chromium as Cr., Mercury, Selenium, lead, Silver, Zinc	individually or in total shall not exceed 1 ppm.

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