QUALITY OF DRINKING WATER IN ZARIA

BY

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D E C L A R A T I O N

I hereby declare that this thesis has been written by me and that it is a record of my own research work. It has not been presented in any previous application for a higher degree. All quotations are indicated and the sources of information are specifically acknowledged by means of references.

Anthony Paul Udoh

March, 1983

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A B S T R A C T

The quality of drinking water in Zaria has been studied. The treated water samples have been collected from different public taps within Zaria and a tap outside the Ahmadu Bello University (ABU) waterworks. In addition, raw water samples were collected from both the Zaria and ABU dams. Chemical analyses include the determinations of pH conductivity, residue (total, filtrable and non-filtrable), chloride, fluoride, iodide and some metals. Sodium and potassium have been determined by Flame Photometry whereas calcium, magnesium, iron, zinc, copper, lead, arsenic and mercury have been determined by Atomic Absorption Spectrophotometry. The results have been compared with the World health Organisation (WHO) standards. The parameters: pH (except values for treated water from the ABU waterworks which fell slightly outside the upper range), conductivity, residue, chloride are present in ranges within the WHO specified limits. Calcium, magnesium, iron, zinc and lead are also found to be present in concentrations within the UHO specified limits whereas copper, manganese, arsenic and mercury are found to be absent in the water samples. Fluoride is found to be present in both the raw and treated samples in concentrations higher than the UHO standard. This makes the water unfit for consumption, especially here in Nigeria where fluoride containing toothpastes of unascertained fluoride contents are generally

used and the fluoride contents of commonly ingested food substances are not known. Iodide has been found in some cases to be present in concentrations higher than the WHO standard.

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A B B R E V I A T I O N S U S E D

ABU = Ahmadu Bello University.

DPD = N,N-Diethyl-paraphenylenediamine.

EDTA = Ethylenediaminetetraacetic acid disodium salt.

m = Mass.

M = Molar.

ppm = parts per million.

P/A = Period's Average.

SPADNS = Sodium 2-(parasulphenylazo)-1,8-dihydroxy-3, 6-naphthalene disulphonate or 4,5-dihydroxy-3-(parasulphenylazo)-2,7-naphthalenedisulphonic acid trisodium salt.

S/N = Sample Number.

V = Volume.

WHO = World Health Organisation.

BMA = British Medical Association.

CHAPTER 1

I N T R O D U C T I O N

1.1 DRINKING WATER - WHY ANALYSIS?

Water, a unique substance, forms a vital and an integral part of a man's life. It is put into very many uses such as drinking, cooking, agriculture, transport, industry and even recreation. Whatever the purpose for which it is required, it has long been recognised that its suitability for such a purpose is affected by the presence of other substances in it. It is for this reason that the chemical examination of water meant for specialised purposes has been carried out over a century ago and in particular, the chemical analysis of water intended for human consumption has formed the subject for analytical texts in the same period (1). If water is dirty, a knowledge of its history and of course its constituents may be of assistance in forming a judgement as to the degree of risk attendant on its employment for domestic use. Though many substances may be permitted to exist in public water supply only to a limited extent, certain properties of the water must be controlled within specified limits to preserve a wholesome and palatable supply (2). The quality of drinking water has attracted the attention of not only the Nigerian Government but the generality of the public and this is

evidenced in the themes of recent conferences (3) and publications (4).

1.2 THE SIGNIFICANCE OF SUBSTANCES FOUND IN WATER

1.21 Acidity

An acid water is one which has a pH value less than 7.0. The most usual causes of acidity are free carbon dioxide and organic acids. Most acid waters are corrosive and the use of lead piping in a distribution system carrying an acid water must always be prevented otherwise, lead, a poison will be taken into solution. The defined limits for the acidity of a water is indicated by the pH range 6.5-9.2. Water with a pH value outside the range is excessively acidic or basic.

1.22 Alkalinity

The cause of alkalinity is the presence of bicarbonates, carbonates and hydroxides of calcium, potassium and sodium. Of these, calcium bicarbonate is the most usual constituent causing alkalinity. Some confusion however occurs in the use of the term "alkalinity" because of the habit of chemists to give two meanings to this word: to denote pH over 7.1 and to denote the total amount of these substances mentioned above which are present in a water. In the latter context, analyses are often quoted "alkalinity as calcium carbonate" (meaning the sum of the constituents mentioned above).

The most usual substances causing alkalinity - calcium and magnesium bicarbonates happen also to cause temporary

hardness. When alkalinity and hardness figures are equal, all the hardness is temporary and is then termed carbonate hardness, when they vary, the excess represents non-carbonate or permanent hardness. If the total hardness is less than the alkalinity, the difference indicates the presence of sodium bicarbonate which adds to the alkalinity but does not increase the hardness (5). This is nearly always due to base-exchange softening including natural softening in deep underground strata (6). The alkalinity of many waters is in the range 100-200ppm; a few waters contain up to 400ppm. No harm comes from the consumption of such waters.

1.23 Chlorine And Chloride

The chlorination of water has often been referred to as "sterilisation." The term is not strictly applicable because it means the destruction of all living organisms including bacterial spores. The more correct term in connection with water treatment is "disinfection" which means a reduction to a low level of the numbers of particular types of organisms. The precise action by which chlorine kills bacteria in water is not known. It is believed that chlorine compounds formed when chlorine is added to water interfere with enzymes in the bacterial cells which are vital for the support of life.

Chlorine is a strong oxidising agent which breaks up organic matter, restrains algal growth and converts iron and manganese to their oxidised forms. When chlorine is added to water free from ammonia and organic matter, hypochlorous acid is formed:

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

The hypochlorous acid is a weak acid and is dissociated into hydrogen (H^+) and hypochlorite (OCl^-) ions - which are together known as"free available chlorine" (7).

If ammonia is present in the water, monochlororamine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3), are formed. The monochloramine and dichloramine are together known as "combined available chlorine." Free available chlorine is many times more powerful than combined available chlorine as a batericide. Since ammonia is often naturally present in water, it is therefore usual to add sufficient chlorine to react with the amount of natural ammonia present and a further dose of chlorine sufficient to create an excess of free chlorine for speedy disinfection.

According to Twort et.al(1974)(8) the maximum amount of free chlorine that may be permitted to remain in a water supply sometimes depends on taste, odour and corrosion that may result. Some water may give taste trouble when only 0.05ppm is left in supply.

The chloride ion, Cl^-, is one of the major inorganic anions in water and wastewater. In potable waters, the salty taste produced by chloride concentrations is variable and dependent on the chemical composition of the water. Some waters containing 250ppm chloride may have a detectable salty taste if the cations are calcium and magnesium. The chloride concentration is higher in waste water than in raw water because sodium chloride is a common article of diet and passes unchanged through

the digestive system. However, a high chloride content harms metallic pipes and structures as well as agricultural plants.

1.24 Nitrate And Nitrite

Nitrates occur naturally in many water supplies. They may also find access to them through sewage (raw or treated effluent). Nitrate and nitrite are most often expressed as nitrogen in nitrate. Waters with a high nitrate nitrogen are known to cause methaemoglobineamia in young infants (9) when used for making up feeds from milk powders but no precise level of danger is known.

1.25 Iodine

Iodine provides an essential cure for goitre - a condition of compensatory increase in size and number of the epithelial cells in the thyroid gland. The disease is brought about by the thyroid stimulating hormone of the pituitary gland in response to a decrease in the amount of circulating thyroxine, an iodine containing hormone (10). Thyroxine stimulates energy production and accelerates the general metabolic reactions including protein biosynthesis. Its deficiency causes reduced metabolic rate and growth failure (cretinism).

Factors responsible for goitre were searched for prophylactic measures and it was traced mainly to low dietary iodine supply (11). The main sources of iodine for a man are drinking water and food. These usually vary in iodine content depending on the availability of this nutrient in water and environmental soil. The inverse relationship between incidence of goitre and

iodine content of drinking and environmental water has been repeatedly emphasised (12-16).

The iodine content of water of a locality is regarded as an important index of the status of this nutrient in the earth's surface and as also in the edible plant and animal products. In 1950, the Nutrition Committee of the British Medical Association recommended 100-150ug of iodine as daily human requirement (17, 18). In 1968, the Food and Nutrition Board of the National Research Council (U.S.A.) fixed this requirement at 75ug (19). It has been shown that an imblanced diet (containing high carbohydrate and low protein, high dietary calcium, polluted water and naturally occurring antithyroid compounds) might raise the requirement of iodine (20, 21). The administration of iodized salt has been advocated and successfully practiced as prophylactic measures against endemic goitre in many affected zones of the world (22).

1.26 Fluoride

Fluoride ions are chemical substances that produce effects on living tissues and in particular, play an important role in the dental system of a man and animals (23). Its supply in drinking water is inversely related to the occurrence of dental caries in a population. According to Scoop(1973) (24), dental cary or tooth decay is a bacterial infection that develops when the mineral components of enamel dissolve in acids formed by bacterial accumulation on the tooth surfaces.

The effects of fluoride ion are inversely related to the amount of fluoride in contact with the living tissue. These

effects may be divided into beneficial and non-beneficial. In man, the former far outweigh the various and rarely occurring non-beneficial (toxic) effects. Fluoride ions exert action on the hydroxyapatite crystal of enamel and cause through their physical presence a decrease in the solubility of enamel in acids and the stabilisation of crystalline structure by providing additional and stronger hydrogen bonds and a promotion of the remineralisation or hardening of the enamel surface. They also exert action on the bacteria of the dental plaque (25). Stiles et al (1976) (26) have shown that the concentration of fluoride ion in the immediate vicinity of the dental plaque organisms can be sufficiently high to inhibit vital microbial enzyme systems and thereby alter the usual pattern of growth and acid production which leads to tooth decay.

Although the high concentration of fluoride in surface enamel and in plaque may be unavoidable since it is in a bound form, it is now known that when attacked by acid (from bacterial fermentation process) the fluoride may be released in ionic form to kill the bacteria.

Fluoridesoccur naturally in many public water-supplies. If present in drinking water in excess of 1.0 to 1.7ppm (27) they may give rise to dental fluorosis with resultant skeletal damage in both children and adults. In assessing the safety of a water supply with respect to the above mentioned limits of fluoride concentration, special consideration should be given to the total fluoride intake by the individual. Apart from variations in climatic conditions, it is well known that in some areas, certain food substances contain fluorides. Consequently, due attention should be given to both factors. Therefore in

those areas where fluoride containing foods are ingested, the lower limit of the above concentration range should be the guiding factor as to the chemical quality of the water. If the fluoride concentration in the drinking water of a population is less than 0.5ppm, a high incidence of dental caries is likely to occur. To prevent the development of this in children, a number of commercial water-supplies are usually fluoridated to bring the fluorine concentration to 1.0ppm (28).

1.27 Hardness

Some materials present in water react with soap causing a precipitate (a scum or curd) to be formed on the surface of the water. Until enough soap has been dissolved to react with all these materials, no lather can be formed. A water which behaves like this is said to be hard. This hardness could be temporary (caused by bicarbonate and removed by boiling) or permanent (non-carbonate or non-temporary and not removed by boiling).

The hardness of a water does not detract from the palatability of the water - on the contrary, many people consider that the sparkling clear hard waters obtained from chalk are second to none for drinking (29). The WHO "highest desirable level" of 100ppm for hardness seems undully low and non-consistent with the corresponding figure of 75ppm for calcium. Very soft waters are liable to dissolve lead (30). Recently, a striking statistical relationship has been found between soft waters and mortality from cardiovascular diseases (31, 32).

1.28 Sulphate

When present in water containing magnesium and sodium, it

gives rise to a bitter taste in the water and causes diarrhea.

1.29 Calcium

It is present in waters as bicarbonate, chloride, sulphate and nitrate. The carbonate is insoluble in water. The bicarbonate is the cause of temporary hardness in water and is present in water from a limestone area. Calcium is an essential ingredient of human diet and is necessary for bone and teeth formation. The required intake of the element is so large that its presence or absence in a water supply is considered immaterial unless the diet is deficient in calcium (33). There is no health objection to a high calcium content in water as many people find hard water very palatable.

1.210 Copper

It is rarely found in natural waters. It may enter water from the use of copper piping or from the use of copper sulphate to reduce algal growth in reservoirs. Though toxic to fish, traces obtained from copper piping are rarely sufficient to affect human beings.

Water containing about 1ppm or less of copper can cause green stains on sanitary fittings and according to Campbell(1971) (34) much lower concentrations can cause accelerated corrosion of other metals in the same system. 0.1ppm of copper is sufficient to increase considerably the rate of corrosion of galvanised steel and as little as 0.02ppm will cause pitting of aluminium in some waters. The WHO "highest desirable level" in drinking water is 1.0ppm and the "maximum permissible level" is 1.5ppm with reference to taste and corrosion and 'green staining' but

without toxic effect to human beings.

1.211 Iron

It is frequently found in raw waters. A large quantity of it can usually be found in all waters delivered to the consumer when the water has been in contact with iron pipes. Iron is an important constituent of haemoglobin which transports oxygen in the body. Though it is not harmful, its presence above a certain amount:

(i) can make water unpalatable, imparting a bitter taste to the water when present in large amounts;

(ii) when the water is exposed to air and takes up oxygen, the iron is likely to precipitate out and deposits cause brown stains upon sinks, baths, washbasins and laundry. Commercial laundries take strong objection to iron in a water.

Iron can be picked up from many underground formations and the waters which contain iron are often corrosive. A water which contains iron is termed "ferruginous."

1.212 Arsenic

Arsenic is a well known toxic element. It has been found to be mutagenic and is associated with chromosomal aberration in man. Any arsenic detected in water is a case for concern and investigation. Arsenic sometimes occurs in the runoff from

waste tips and from catchments containing metalliferrous ores. It also has been used in some sprays for weed killing and arsenical solutions are used for sheep dipping. A water authority should keep a watch on any catchment for use of arsenic: it is frequently prohibited from use in sheep dips on reservoir catchments. However, a note in 'International standards' states that high figures are found in a number of Latin American countries and levels up to 0.2ppm are not known to have caused difficulties (35).

1.213 Aluminium

Aluminium is found in some natural waters in a detectable amount; it can also enter a water from the use of aluminium cooking untensils, tanks or pipes. There is however no evidence that the use of aluminium cooking utensils has caused harm to consumers. The corrosion of aluminium can, however, be caused by a copper-bearing water, even if the copper content is very small. Thus, care must be taken not to supply water through long lengths of copper pipe to an aluminium tank. Occasionally other waters which are alkaline and contain sodium carbonate cause corrosion of aluminium; this corrosion taking the form of pitting of the metal.

Another source of aluminium in a water supply arises from the incorrect dosing of aluminium sulphate as a coagulant at the treatment works. This should not occur and there should be no tendency for deposition of aluminium hydroxide after a water has been properly treated by filtration and the filtrate should not contain more than 0.15ppm aluminium.

1.214 Lead

This element is a well known poison and is rarely

detectable in natural waters even using the most modern method sensitive to 0.02ppm (except when they are affected by discharges from mines) (36). The WHO 'International Standards', 1971, tentative limit of 0.1ppm thus seems unnecessarily permissive if it is intended for application to water at the pumping station; no water undertaking would be justified in supplying water with that amount. The WHO 'European Standards', 1970, suggests a maximum of 0.3ppm after 16 hours contact with lead pipes and usefully mentions the possibility of it also being leached out of certain plastic pipes. For any doubtful waters, determinations of lead content should be made in the water obtained from consumer's taps, both under normal running conditions and in the first drawoff after standing overnight under normal running conditions, the concentration should be less than 0.05ppm.

1.215 Magnesium

In combination with bicarbonate and sulphate ions, it causes hardness. The advantages and disadvantages of hard water have been earlier mentioned.

1.216 Manganese

It is a troublesome element in water even when present in small quantities. In the presence of oxygen or when chlorine is added, it tends to deposit out from water thereby coating the interior of pipes as black slime. The slime eventually gets detached from the pipewalls and is conveyed through the service pipes to the consumer's premises where it is most objectionable.

Manganese is often associated with iron in a water and has a behaviour which is similar, except that the deposits are cumulative. High quantities of manganese are toxic but long before such a level is reached in a public supply, treatment must be installed to reduce the nuisance created. Well waters contain a troublesome amount of manganese and in countries where there are impounding reservoirs, the bottom water may take up manganese from the reservoir floor soil or deposits so that an increase of the manganese content of the supply may occur in spring and autumn when reservoir 'overturn' (remixing) is likely to occur (37). Generally, a lesser amount of manganese can be tolerated in a supply system than iron because, though deposition of manganese is slow, it is continuous and the onset of serious troubles may not be apparent for some ten to fifteen years after adopting residual chlorination as a policy. About 0.5ppm manganese may be regarded as the upper limit but it is quite possible for a lesser quantity to cause trouble in a distribution system.

1.217 Zinc

It is rarely present in natural waters but very common in water when it is drawn from consumer's taps because of the use of galvanized iron piping and tanks. Some waters may attack the zinc of galvanized piping forming loose zinc carbonate; and this zinc in solution in such waters as supplied to the consumer may be found to exist up to 3.0ppm. Samples containing such amounts of zinc should be avoided for bacteriological examination, because zinc has a bactericidal action continuing in the sample bottle, being toxic to many low forms of life but

relatively harmless to human beings.

1.218 Silica

Silica exists in most waters, up to 40ppm (as SiO_2) in hard waters. The content of a river water may fluctuate from 5 to 20ppm. No evidence has been adduced that amounts of the above order or more are harmful for drinking and no permitted limits have been quoted. It is however a troublesome material in boiler feed waters giving rise to a very hard scale (38).

1.219 Sodium

It ranks sixth among the elements in order of abundance and is present in most natural waters as sodium chloride. The ratio of sodium to total cations is important in agriculture and human pathology: a high sodium ratio harms soil permability while persons afflicted with certain diseases require water with low sodium concentration. If the sodium chloride does not arise from sewage pollution but comes from a non-dangerous source it may be tolerated in a water supply up to the level about 300ppm or above at which complaints of taste could arise.

Sodium bicarbonate is a salt present in some waters from 20 to 500ppm and water containing the higher amounts is sometimes regarded as "table water" drunk for its palatability.

Sodium sulphate is the chief constituent of 'sulphated' water and is regarded as harmless even when present in amounts up to 250ppm. Quantities above this may cause diarrhea (39).

1.220 Potassium

It ranks the seventh among the elements in order of abundance but its concentration in most drinking water is 20ppm (40). Just like sodium, it plays a very important role in nervous communications.

1.221 Mercury

It is a comparatively rare element. Its inorganic compounds are relatively insoluble and can exist in solution only in extremely small concentrations under natural conditions. It causes death and nerve damage. It enters water as waste from electrolytic sodium hydroxide production and from the leaching of coal ash. It may be methylated by bacterial activity and taken up by the aquatic food chain to which it is also toxic.

1.3 SOURCES OF DRINKING WATER

There are different sources of drinking water depending on the geographical features of an area. Such sources include small streams, rivers, ponds, springs, rain water (seasonal), wells, boreholes and tap water. Stagnant pond water and wells form the major sources in almost all communities except in urban areas where tap water is available. However, with the growing need for a good quality of drinking water, the tap water system is spreading to even the most remote areas of Nigeria.

1.4 CHEMICAL TREATMENT OF WATER FOR PUBLIC SUPPLY

Varying amount of treatment is usually given to public water supplies before entering the distribution system. In this

process, a continuous supply of raw water is a necessity. The raw water is usually abstracted from some natural waters e.g. rivers and stored in reservoirs (often called dams) and lakes. These are always variedly polluted. The various aims therefore, for treating raw water include the following:

(1) reduction of the total micro-organism content and the removal of bacteria and viruses harmful to health;

(2) removal of chemicals that are harmful to health;

(3) removal of suspended matter;

(4) reduction to a low level of those chemicals that might interfere with the normal domestic and industrial uses of water;

(5) removal of any corrosive properties of water and the protection of the piped distribution system.

The impurities that are present in raw water may be grouped into: floating and suspended solids of visible size; small suspended and colloidal solids causing turbidity, micro-organisms, dissolved solids producing hardness and acidity and dissolved gases such as oxygen, carbon dioxide and hydrogen sulphide.

The treatment of water is aimed primarily at removing most of these impurities. The methods that are used for

treatment are related to the particle size and chemical composition. Treatment procedures are not standardised across different water authorities. They vary according to the quality of the raw water and the extent of water purification required. In the ongoing discussion, particular attention is paid to the Zaria and the Ahmadu Bello University waterworks. The former gets its raw water supply from the Zaria dam which originates from a river near Kano while the latter gets its supply from the Ahmadu Bello University dam.

The chemical treatment of water for public supply is brought about in stages:

(a) chemically assisted sedimentation:

This stage comprises several separate processes of treatment which go to make up the complete system known as "clarification". The system is designed to clear a water as much as possible and desirable of suspended materials before it passes to rapid gravity filters. It is a delicate and chemically complex phenomenon having three stages:

(i) the addition of measured quantities of chemicals to water and their thorough mixing;

(ii) the formation of a precipitate which coalesces or coagulates and forms a floc and

(iii) sedimentation.

In the first stage, energy is applied in some form to make the selected chemicals mix with the water. A "flash mixer" is frequently used which causes the water to have a turbulent flow, either by injecting a stream of high velocity water into it or by passing the water around baffles or through some constriction. At the Zaria and the Ahmadu Bello University waterworks, the water is passed through baffles.

In the second stage known as "floccu-lation", the aim is to achieve the formation of a floc consisting of the precipitate formed by the addition of the chemical to the water combined with particles of suspended matter originally existing in the water. The most widely used precipitate is that formed by the addition of aluminium sulphate, $Al_2(SO_4)_3$, to the water and this is generally known as "alum floc". Practically, equal volumes, say, 500ml of raw water from the source are treat-ed with different concentrations - 5%, 10%, 15%, 20% solution of aluminium sulphate depending on the turbidity of the water followed by rigorous stirring. The concentration that produces the best result is used for treat-ment. The raw water from the source is then pumped into the mixing chamber into which the

correct solution of aluminium sulphate is poured. (Other coagulants which may be used include sodium aluminate, $NaAlO_2$; iron (II) sulphate heptahydrate, $FeSO_4.7H_2O$). The precipitate formed will first consist of very fine particles, and the aim is to make them coalesce (or coagulate) to form larger particles of floc which are more effective in entraining the suspended matter in the water.

In the third stage, the water is provided with a period during which the floc may fall out of the water to the base of some sedimentation tank, or is made to collect together in a layer or "blanket", so that it may be drawn off. These tanks are generally known as "clarifiers".

(b) Filtration

Sedimentation brought about with or without chemical coagulation is usually followed in a waterworks by filtration. Poorly filtered water is backwashed by emptying the tank so that the water level becomes very low. Air at a very high pressure is then passed in from the bottom. This mixes the water with the bed material so that the water becomes turbid. More water is then passed in from the top to wash the bed and then flushed off.

(c) Application of chlorine

Commercial chlorine is delivered as a liquid under pressure in cylinders or drums or it may be brought to the site in bulk tankers which discharge to large pressure vessels in the treatment works. (Chlorine is normally manufactured from salt. In some areas of the world, it may be difficult or expensive to obtain commercial chlorine in liquid or gas form. In this case, electrolytic sodium hypochlorite generators can be used to manufacture sodium hypochlorite solution at the site of the works from brine solution or from sea water. The apparatus is not expensive to instal and the power consumption is modest). The chlorine cylinders usually contain about 30kg (70lb) of liquid chlorine in them, the drums about 800kg (1800lb). In a very large waterworks, the chlorine gas is stored in much larger vessels which are refilled from tankers. The chlorine is not usually injected straight from the containers into the water because

(i) the dose to be applied must be controlled;

(ii) the dose must remain constant whatever the pressure inside the cylinder (the pressure tends to fall as the gas is withdrawn and varies according to temperature).

(iii) if the water is under pressure, it may be necessary to force the gas into it.

For emergency, one can discharge the chlorine direct into the water provided every precaution is taken to see that all the gas is dissolved in the water and none escapes. However, for all normal operating circumstances, it is necessary to use a chlorinating apparatus which controls and measures the gas applied. The chlorine is normally applied as a concentrated solution by allowing the chlorine to flow through an orifice and mix with a small quantity of water to form a concentrated solution which is passed on to the injection point. The amount of chlorine added usually depends on the result of post-treatment test. At the Zaria waterworks, 2.0kg/hour chlorine is added.

It is more convenient to inject the chlorine into water where the pressure is not too high. The primary requirement is that any point of application must be such as to give adequate time of contact for the chlorine with the water before it leaves the works or before the water is dechlorinated (this can be brought about by injecting sulphur dioxide). Preferentially, the point of application should be just upstream of a weir or venturi tube or some other similar point where turbulence of the water

will ensure thorough mixing of the chlorine. Aeration after the addition of chlorine is not objectionable as it will only reduce the chlorine content by a very small amount but long exposure to sunlight will result in a decrease of the chlorine content.

(d) Addition of other chemicals

At the waterworks, other chemicals are usually added to the water at this stage. Thus, along with the chlorine is usually added ammonium sulphate solution. The chlorine combines with the ammonium sulphate to form the chloramines earlier referred to. Calcium oxide solution is used at this stage to regulate the pH of the water.

At the Zaria waterworks (and most others) the treated water is stored in underground tanks (reservoir) from where the water may be pumped into various distribution tanks. The amount of chlorine gas present in the treated water as compared to the added quantity is tested for at definite intervals using o-toluidine or D.P.D. tablets. This usually indicates the amount of residual chlorine present in the water although this decreases greatly by the time the water gets to the consumers.

A salt, sodium alginate, is also added to

the raw water along with aluminium sulphate. This salt helps in coagulation. Both the Zaria and the Ahmadu Bello University water-works and even most others, do not use it because it is said to encourage the growth of algae as well as blocking the pipes. The Zaria waterworks pumps out about eleven million gallons of treated water a day.

5 OBJECTIVES OF THE PROJECT

This work is aimed at the quality characterisation of tap water in Zaria. This water is supplied to the public by the Zaria waterworks. Apart from the joy and satisfaction resulting from an exercise like this, it is hoped that from the results of this analysis, both the public and the various water works in the country will become increasingly aware of the need to maintain a constant check at the constituents of the tap water they supply to the public.

It has already been mentioned that raw water depending on its source is varyingly polluted. It may contain among other things substances like chloride, fluoride, iodide, sodium, potassium, calcium, manganese, magnesium, aluminium, iron, copper, lead, zinc, silica etc. which occur naturally.

In the pursuance of the above objective, determination of the following substances will be carried out on both raw and treated water:

(a) pH, conductivity, residue (total, filtrable and suspended);

(b) chloride, fluoride and iodide;

(c) sodium, potassium, calcium, magnesium, iron, zinc, copper, lead, manganese, arsenic and mercury. The results will be compared with the WHO standards.

CHAPTER 2

SAMPLING AND DETERMINATIONS

2.1 SAMPLING - GENERAL

The validity of an analytical result depends on the efficiency of sampling. The general locations for obtaining the samples should be dictated by the objectives of the programme. Sometimes, the objectives may be such that the exact sampling locations remain to be chosen but it is generally better to ensure that the locations at which the samples are taken are representative of the water of interest. In some analyses, sampling positions seem to be chosen more on the bases of accessibility and convenience than on their suitability as representative samples (41). This may sometimes be unavoidable but it is always worth seeking an alternative position if the one that is accessible is likely to provide information of uncertain value.

2.11 Frequency Of Sampling

Tap water was used for this project. Samples were collected forthnightly in September and October and thereafter weekly up to early December 1982. The period cut across the later part of the rainy and the early part of the dry seasons. Altogether, samples were collected ten times and analysed.

2.12 Sampling Positions

Samples for this project were collected from different points within Zaria. The different points were determined by the number and position of distribution tanks that serve water to the entire Zaria community. After treatment, water from the Zaria waterworks is pumped directly into the two Kanwa tanks which serve as the central reservoir. From these, the water is pumped directly into the different booster tanks located in different communities.

The Ahmadu Bello University community gets its water supply from the Zaria public water supply system. Though the University has a waterworks which serves at present only a negligible section of the University community, construction work is now being carried out in order to make it possible for the whole University community to get its water supply from the University waterworks. This necessitated the inclusion of both the raw water from the University dam and the treated water from the University waterworks now that the treated water from the latter is not yet widely used and whereupon the findings could be more useful. The raw water from the Zaria dam was also included in this study so as to be able to observe any changes that may occur in the concentration of determinants in both raw and treated water samples. Details of sampling points are given in Tables 2.1 and 2.2 below.

Table 2.1

Zaria Public Water System

Tank Location	Area(s) Served	Sampling Point	Sample Number
Hanwa tanks	Central Reservoir	-	-
-	-	Zaria dam	1
-	-	Tap outside Zaria waterworks	2
City tank	Tudun Wada/ Zaria City	Kongo	3
Gaskiya tank	Tudun Jukun	A88 Gaskiya Road	4
Supply from different tanks around	Sabon Gari	2 Yoruba Street	5
G.R.A.	G.R.A. and surroundings	Zaria Polo Club	6
Samaru	Samaru, Shika	8 Sokoto Road, Samaru	7
Kufena tank	Wusasa and surroundings	Wusasa General Hospital	8

Table 2.2

Ahmadu Bello University Water System

Tank Location	Area(s) Served	Sampling Point	Sample Number
A.B.U. Waterworks	Parts of Area A	Tap outside waterworks	9
-	-	A.B.U. Dam	10

2.13 Time Interval Between Sample Collection And Analysis

In an analysis such as that involved in this project, the shorter this time interval the more reliable the results (42, 43). For some constituents and physical values, immediate analysis in the field is required in order to obtain dependable results because the composition of the samples may change before they are brought to the laboratory. Though the WHO has stipulated a period not exceeding 72 hours (44), it is impossible to state unequivocally how much time may be allowed to elapse between collection and analysis as this depends on the character of the sample, the particular analysis to be made, the storage conditions and the distance between the sampling points and the laboratory.

In this work, no parameter was determined in the field. Analyses were started immediately the samples were brought to the laboratory. Approximately four hours were used to collect all samples during each outing.

2.14 Sample Collection And Preservation

Samples were collected into plastic containers soaked overnight in a 10% V/V nitric acid solution (45). A complete and unequivocal preservation of the samples is often practically impossible. Similarly, irrespective of the nature of the sample, complete stability for all constituents can never be achieved. Preservation methods only retard chemical and biological changes which inevitably continue after the sample has been removed from the source. Such chemical changes may include cation loss by adsorption on or ion exchange with the

walls of the container e.g. zinc, copper, lead, chromium, if the container is glass. Such solutions are usually kept at pH below 2.0 using hydrochloric or nitric acids to reduce precipitation and adsorption on the container walls. In addition to the above effect certain metal ions may change their oxidation states e.g. chromium (IV) being reduced to chromium (III).

The biological changes such as those caused by the growth of organisms may be retarded by keeping the sample in the dark at low temperatures until analysis. However, certain determinations are more likely to be affected than others by the storage of the samples prior to analysis. Such determinations include temperature which changes very quickly, the pH which may change significantly as a matter of minutes and dissolved gases (oxygen, carbon dioxide, hydrogen sulphide, chlorine) may be lost or gained.

Due to the treatment normally given to tap water at the waterworks, much biological activities apart from oxygen and carbon dioxide exchange do not occur but common among changes in drinking water are the conversion of soluble constituents to organically bound materials in cell structure or the release of cellular materials into solution. This biological influence on the sample composition is exemplified by the nitrogen and phosphorus cycles (46).

It is difficult to preserve samples since almost all preservatives interfere with some analyses. Though a number of preservation methods have been suggested (47), they are relatively limited and are intended to retard biological

action, the hydrolysis of compounds and complexes and reduce constituent volatility. No special method of sample preservation was used in this work and all analyses were completed within one week of sample collection.

2.2 DETERMINATIONS

2.21 pH Determination (48, 49)

Principle: pH is widely used as a general characteristic of a water and an indirect estimation of carbon dioxide quantities. The pH of a water sample is liable to be modified by biological activity or by carbon dioxide exchange with air, long intervals exceeding a few hours between collection and measurement should be avoided and samples should be collected in completely filled vessels. For accurate determinations, a preliminary flushing of the vessel with the sample is often necessary.

The glass electrode-calomel electrode system is most conveniently used as a single combination electrode that can be dipped into the sample vessels. A preliminary stirring of the medium or agitation of the electrode is essential before a reading is taken, although it should be noted that a lower reading will be obtained during the stirring.

The meter plus the electrode system are usually standardised before measurement, using, preferably, buffer solutions with pH values near the upper and lower limits of the range to be measured and the sample temperature.

Apparatus: (1) pH meter (battery operated), Griffin. (2) Combination glass-calomel electrode, Gallenkamp. (3) 500ml beaker. (4) Magnetic stirrer.

Procedure: The storage vessel was removed from the pH sensitive membrane thereby exposing the membrane and the reference liquid junction. The membrane was washed with de-ionised distilled water and wiped with soft tissue. The electrode was then checked to ensure that the internal liquid solution completely filled the pH sensitive membrane. If air bubbles were present, these were removed by shaking the electrode in a downward direction. The silicone band covering the salt bridge was slided down to expose the hole thus ensuring the diffusion of the electrolyte through the ceramic liquid junction. The electrode was then standardised in buffer solutions of pH 6.0 and 10.0. The buffer solutions bracketted the expected pH range of the test samples. The specified sampling procedure was then carried out, washing the electrode after each immersion into the solution under test to prevent contamination of the test samples and the buffer solutions. After use, the electrode was cleansed with more of deionised distilled water and the protective cap replaced. The electrode was then stored in a buffer solution of pH 7.0. The pH meter used in this work was not adapted to temperature regulation. Full results are shown in Appendix III(a) and summarised results are included in Tables 3.1 to 3.4.

2.22 Conductivity (50, 51)

Principle: Electrolytic conductivity is the ability of a solution to conduct an electric current. In solution, electricity is carried by ion migration. Therefore conductivity under standard conditions (electrode geometry and temperature) bears some relationship to the total ion concentration. To some extent, this relationship depends on the nature of the major ions in solution so that water of different ionic composition will display a different relationship between ionic concentration and conductivity. Unfortunately, conductivity tells us nothing as to the nature of the substances in solution but if this increases or decreases in amount, so does the conductivity increase or decrease and if the conductivity of the water is ascertained, then any change in the character of the water will be indicated by a change in the conductivity.

The S.I. unit of conductivity is the siemens (S), and the inverse of the unit of Electrical Resistance (R), the ohm (Ω). For electrolytic solutions, conductivity (K) is expressed as μscm^{-1}, a value numerically equivalent to $\mu mho\ cm^{-1}$ (in older literature).

Apparatus: Electrolytic conductivity measuring set, Model MC-1, Mark v, Electronic Switchgear, London Ltd., England.

Procedure: The cell was cleansed thoroughly with de-ionised distilled water followed by the sample to be measured. The cell was then filled with the sample and the connecting cable plugged into the "measuring cell" socket. The temperature dial was set to the temperature of the sample (25°C) and the

selector switch to the anticipated range of measurement (by trial). The actuator button was pressed down and the measuring dial slowly rotated until the balance indicator moved to the centre scale. The dial setting at which this occured was read and multiplied by the range factor. The result was the specific conductivity of the sample in $uscm^{-1}$. Summarised results are included in Tables 3.1 to 3.4 while full results are shown in Appendix III(b).

2.23 Determination of residue (52, 53, 54)

Residue, as a chemical term, refers to solid matter suspended or dissolved in water. The material left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature is called "total residue". It includes "non-filtrable reside", that is, the portion of total residue retained by a filter and "filtrable residue", the portion of the total residue that passes through the filter. Practically, however, the distinction between "filtrable" and "non-filtrable" components is an operational rather than an absolute one, and can be influenced by the grade of filter employed.

2.231 Determination of total residue dried at 103°-105°C

Principle: A well-mixed sample is evaporated in a weighed evaporating dish and dried to constant weight in an oven at 103°-105°C. The increase in weight over that of the empty dish represents the total residue, an arbitrary quantity defined by the procedure followed. The determined values may not check with the theoretical value for solids calculated

from the chemical analysis of water.

Experimental

Apparatus: (1) Porcelain evaporating dishes of 100ml capacity and 90mm diameter. (2) Steam bath. (3) Drying oven equipped with a thermostatic control capable of maintaining the temperature within a 2°C range. (4) Desiccators containing silica gel desiccant. (5) Analytical balance, 160g capacity capable of weighing to 0.1mg.

Procedure: Clean porcelain evaporating dishes were kept in an oven set at 103°-105°C overnight. These were then cooled in desiccators and weighed. 25ml portion of the sample was then pipetted into a dish and evaporated to dryness on a steambath. The evaporated sample was then dried in the oven at 103°-105°C for 1 hour. This was cooled in a desiccator and weighed. The processes of drying, cooling in a desiccator and weighing were repeated until a constant weight was obtained. Triplicate determinations were carried out simultaneously for each sample and average results were used in the calculation.

Calculation: The following expression was used:

$$\text{mg/l total residue} = \frac{(A-B) \times 1000}{\text{ml sample}}$$

where

A = weight of sample + dish;

B = weight of dish only.

Summarised results are included in Tables 3.1 to 3.4 while full results are shown in Appendix III(c).

2.232 Determination of filtrable residue dried at 103°-105°C

Apparatus: In addition to those already mentioned for total residue, the following: (1) Suction flasks (500ml capacity) with rubber bung. (2) Sinter glass filter, size G3, Pyrex. (3) Suction pump.

Procedure: A suction flask connected to the suction pump was fitted with a rubber bung carrying a sinter glass filter, size G3 pyrex. The suction pump was connected to the mains and switched on. The sinter glass was washed with three successive 20ml volumes of distilled water. Suction was continued to remove all traces of water from the filter and the washings discarded. About 50ml of the sample was then filtered under vacuum. The filtrate was used to rinse the suction flask. About 100ml of the sample was then filtered by the same procedure. 25ml aliquot of the filtrate was pipetted into a preweighed evaporating dish (dried in the oven at 103°-105°C and cooled in the desiccator) and evaporated to dryness on a steam bath. The evaporated sample was then dried in the oven at 103°-105°C for 1 hour. It was cooled in a desiccator and weighed. Drying, cooling and weighing were continued until a constant weight was obtained. Triplicate determinations were carried out simultaneously for each sample and average results were used for the calculations.

Calculation: The following expression was used:

$$\text{mg/l filtrable residue} = \frac{A-B \times 1000}{C}$$

where

A = weight of dish + dried residue,

B = weight of dish only,

C = volume of filtrate used.

Summarised results are included in Tables 3.1 to 3.4 while full results are shown in Appendix III(d).

2.233 Determination of suspended residue at 103°-105°C

Procedure: This was determined for each sample from the relationship:

Total Residue	=	Filtrable Residue	+	Suspended Residue

The method proved useful since the same volumes of samples were used in the determinations of total and filtrable residues. Summarised results are included in Tables 3.1 to 3.4 while full results are shown in Appendix III(c).

2.24 Determination Of Chloride (55, 56, 57, 58, 59, 60)

A number of methods are available for the determination of chlorides in water. These include the argentometric (Mohr), the mercuric nitrate, the potentiometric and the ferricyanide methods.

The potentiometric method is suitable for coloured (turbid) samples in which colour-indicated end points are

difficult to observe but can be used without a pretreatment step for samples containing ferric ions (if not present in an amount greater than the chloride concentration). The ferricyanide method is an automated modification and is tentative. The mercuric nitrate method has an easier end point but is very much pH (difficult to maintain) dependent.

The argentometric method is suitable for use in relatively clear waters and was the procedure adopted for this work. The method avails itself of the well known reaction of silver salts on soluble chlorides. When a solution of the nitrate of silver is mixed with a solution containing chlorides, the insoluble chloride of silver is produced and the quantity of chloride in water may be determined by ascertaining how much of a standard solution of nitrate of silver is required, in order to precipitate all the chloride in a certain volume of the water sample.

If some of this standard solution be dropped into a water containing chloride, a white precipitate of chloride of silver will continue to form until all the chloride in the water has been used up. As may be readily seen on making the experiment, there is some difficulty in observing the exact point at which the formation of the precipitate ceases. The difficulty is overcome by using potassium chromate as indicator. By employing this, the exact point at which the formation of chloride of silver stops is marked by the appearance of a deep red chromate of silver. The principle upon which the indicator depends is, that silver combines with chloride in preference to chromic acid and that, accordingly, no red chromate of silver

is capable of being formed so long as chlorides are in the water, but that red chromate of silver instantly forms the moment the nitrate of silver is in the slightest excess.

In this experiment, both the silver nitrate and potassium chromate should be free from chloride. Also, neither the silver nitrate nor the water sample should be acidic. This is because the chromate of silver is dissolved by acids.

Experimental

Reagents: All chemicals were of analytical reagent grade unless otherwise stated.

(1) Chloride-free water: Deionised distilled water was used for the preparation of all reagents and as dilution water.

(2) Potassium chromate indicator solution: This was prepared by dissolving 50g potassium dichromate (analytical grade reagent) in a little quantity of water followed by the addition of silver nitrate solution until a definite red precipate was formed. This was left to stand for 12 hours, filtered and diluted to 1 litre.

(3) Standard silver nitrate titrant (0.0141M): Prepared by dissolving 2.395g silver nitrate in water and diluting to 1 litre. The solution was standardised against 0.0141M sodium chloride solution by the procedure described below and stored in a brown bottle. Standard silver nitrate 0.0141M = 500µg Cl/ml.

(4) Standard sodium chloride (0.0141M) solution: Prepared by dissolving 824.1mg sodium chloride (dried at

140°C) in a small quantity of water and diluting to 1 litre. 1.0ml = 500µg Cl.

(5) Special reagents for the removal of interference: (i) Aluminium hydroxide suspension: Prepared by dissolving 125g aluminium potassium sulphate ($AlK(SO_4)_2.12H_2O$) in water and diluting to 1 litre with more of the water. The solution was warmed to 60°C and 55ml ammonia solution was added slowly with stirring. The mixture was left to stand for 1 hour and transferred to a large bottle. The precipitate was washed by successive additions, with thorough mixing and decantations of water until free from chloride. A feshly prepared suspension occupies a volume of approximately 1 litre. (ii) Phenolphthalein indicator solution: Prepared by dissolving 1g of the solid in 500ml ethanol and diluting to 1 litre with water. (iii) Sodium hydroxide (1M) solution: Prepared by dissolving 40g sodium hydroxide pellets in a small volume of water and diluting with more of the water to 1 litre. (iv) Hydrogen peroxide, H_2O_2, 30% v/V: Prepared by diluting 30ml of hydrogen peroxide to 1 litre with deionised distilled water. (v) Sulphuric acid (0.05M): Prepared by diluting 2.8ml concentrated sulphuric acid to 1 litre with water.

Procedure: (a) Sample preparation: 10ml sample was diluted to 100ml with water. Raw water samples were treated with 3ml aluminium hydroxide suspension, mixed, left to settle, filtered, washed and the filtrate and washings combined.

(b) Titration: Samples were titrated in the pH range 7.0 to 10.0 directly. Samples not in this range were

adjusted with sulphuric acid or sodium hydroxide solutions. 1.0ml potassium chromate indicator solution was added and the resulting solution titrated with the standard silver nitrate titrant to a pinkish yellow end point.

A reagent blank value was established by titrating the standard silver nitrate solution with 100ml deionised distilled water by the method outlined above.

Calculation: The following relationship was used:

$$mg/l\ Cl = \frac{A-B \times N \times 35,450}{ml\ sample}$$

where

A = ml titration for the sample

B = ml titration for the blank

N = Molarity of silver nitrate solution.

The summarised results are included in Tables 3.1 to 3.4 while full results are indicated in Appendix III(f).

Table 2.3

Interferences In The Mohr Method For Chloride (61)

Interfering Species	Comments
Br^-, I^-	-
Fe(III), Bi(III), Sn(IV)	Precipitated as basic salts; interference by Fe(III) partially removed by addition of F^-.
Ni(II), CO(II), Cu(II)	Mask colour.
$S_2O_3^{-2}$, S^{-2}, CO_3^{-2}, $C_2O_4^{-2}$	Interfere by formation of low solubility silver salts in neutral solution. $C_2O_4^{-2}$ can be precipitated as calcium oxalate.
NH_4^+	pH adjustment will overcome interference. Optimum pH is 5.0-8.0

Interference by the last two groups was overcome by the high pH of the solutions (7 to 10) before titration. Interference by iron(III) is overcome by fluoride naturally present in samples. Most of the other metal ions are not significantly expected to be present in the samples.

2.25 Determination Of Fluoride (62, 63)

Many methods have been suggested for the determination of the fluoride ion in water: the electrode method, the alizarin visual method, the alizarin fluorine blue method, the Zirconium-Eriochrome cyanine R method and the Zirconium-SPADNS method. The electrode method is based on its response to the fluoride ion. This electrode response is however dependent on the ionic strength of the test solution or sample. This selective ion technique shows promise as a versatile adjunct to the colourimetric measurement of fluoride ion with a special advantage possibly in situations requiring continuous monitoring or with large concentration differences.

The alizarin visual method depends largely on the ability of the analyst to discern between colours. Though it requires inexpensive laboratory glassware and does not require accurate time control because sample and standards are treated simultaneously under the same conditions, a waiting period of 1 hour after reagent addition is however suggested as satisfactory for colour development. Such visual methods have been discarded in favour of methods adapted to photometric measurement.

The last three methods are colourimetric (photometric). The SPADNS (and even the electrode) methods allow measurements to be made at any time after reagent addition and the former was used in this work. In this procedure, the reaction rate between fluoride and zirconium ions is influenced greatly by the acidity of the reaction. By increasing the proportion of acid in the reagent, the reaction is made practically

instantaneous. The selection of the dye for this rapid fluoride method is governed largely by the resulting tolerance to interfering ions. The electrode and the colourimetric methods are the most satisfactory at the present time. The colourimetric methods are based on the fluoride ion activity upon a colour producing reaction, usually between a metal and an organic dye. Nearly all such reactions result in an inverse relationship - a decrease in colour intensity with increasing fluoride concentration. Since all the colourimetric methods are subject to errors due to interfering ions, it may be necessary to distil the sample before making the fluoride determination. However, when the interfering ions are not present in excess of the tolerances of the method, the fluoride determination may be made directly without distillation.

Experimental

Apparatus: Colourimetric equipment: An EEL spectrophotometer for use at 570nm and providing a light path of at least 1cm.

Reagents: All chemicals were of analytical reagent grade.

(1) Deionised distilled water was used for the preparation of all reagents and as dilution water.

(2) Stock fluoride solution: Prepared by dissolving 221.0mg anhydrous sodium fluoride, NaF, in water and diluting to 1 litre with more water. (1ml = 100μgF i.e. 100ppm stock solution).

(3) Standard fluoride solution: Prepared by diluting

100ml of the stock fluoride solution to 1 litre with water. (1.0ml = 10.0μgF i.e. 10ppm standard solution).

(4) SPADNS solution: Prepared by dissolving 1.916g SPADNS in water and diluting to 1 litre with more water. This solution is stable indefinitely if protected from direct sunlight.

(5) Zirconyl-acid reagent: Prepared by dissolving 266mg zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$, in about 50ml water. To this was added 700ml concentrated hydrochloric acid and the solution diluted to 1 litre with water.

(6) Acid Zirconyl-SPADNS reagents: Prepared by mixing equal volumes of SPADNS solution and Zirconyl-acid reagent. The combined reagent is stable for at least two years.

(7) Reference solution: Prepared by adding 10ml of SPADNS solution to 100ml water. 7.0ml concentrated hydrochloric acid was diluted to 10ml with water and added to the diluted SPADNS solution. The resulting solution, used for setting the reference point (zero) of the spectrophotometer, is stable and may be reused indefinitely.

(8) Sodium arsenite solution: Prepared by dissolving 2.50g sodium arsenite, $NaASO_2$, in a small volume of water and diluting to 1 litre with more water.

Procedure: (a) Preparation of standard curve: Fluoride standards in the range 0 to 1.4ppm were prepared by diluting appropriate volumes of the standard fluoride solution to 50ml with water. 10ml of the mixed acid-Zirconyl-SPADNS reagent

was added from a burette to each standard and mixed well. The spectrophotometer was set to zero with the reference solution and the percent transmittance readings of the standards taken immediately. A curve of fluoride concentration-absorbance relationship, Figure 2.1, was plotted. This calibration curve was checked during subsequent determinations.

(b) Sample pretreatment: 50ml of each water sample was used. To each tap water sample was added one drop of sodium arsenite solution and the mixture stirred well to remove any residual chlorine present. Raw water samples were not treated with sodium arsenite solution.

(c) Colour development: 10.0ml of the mixed acid-Zirconyl-SPADNS reagent was added from a burette to each sample. The solutions were well mixed, covered and the absorbance readings taken about six hours afterwards with the reference point of the photometer set as for the standards above. Duplicate determinations were carried out for the samples.

Calculation: The following expression was used.

$$\underset{w}{mg/l\ F} = \frac{A}{ml\ sample}$$

where A = ugF determined photometrically

ml sample = volume of sample used

Summarised results are included in Tables 3.1 to 3.4 while details are shown in Appendix III(g).

Table 2.4

Interferences In The Zirconium-SPADNS Method For Fluoride (63)

Interferer	Concentration mg/l	Effect on Fluoride Value mg/l	Removal
1. Alkalinity (as $CaCO_3$)	5000	decreases 0.1	
2. Al^{+3}	0.1	decreases 0.1 on immediate reading	tolerance increases to 3.0 after 2 hours standing and 30 after 4 hours of standing
3. Residual chlorine	-	-	sodium arsenite solution
4. Cl^-	7000	increases 0.1	present below limit
5. Fe(III)	10	decreases 0.1	present below limit
6. $(NaPO_3)_6$	1	increases 0.1	not determined
7. PO_4^{-3}	16	increases 0.1	not determined
8. SO_4^{-2}	200	increases 0.1	present below limit

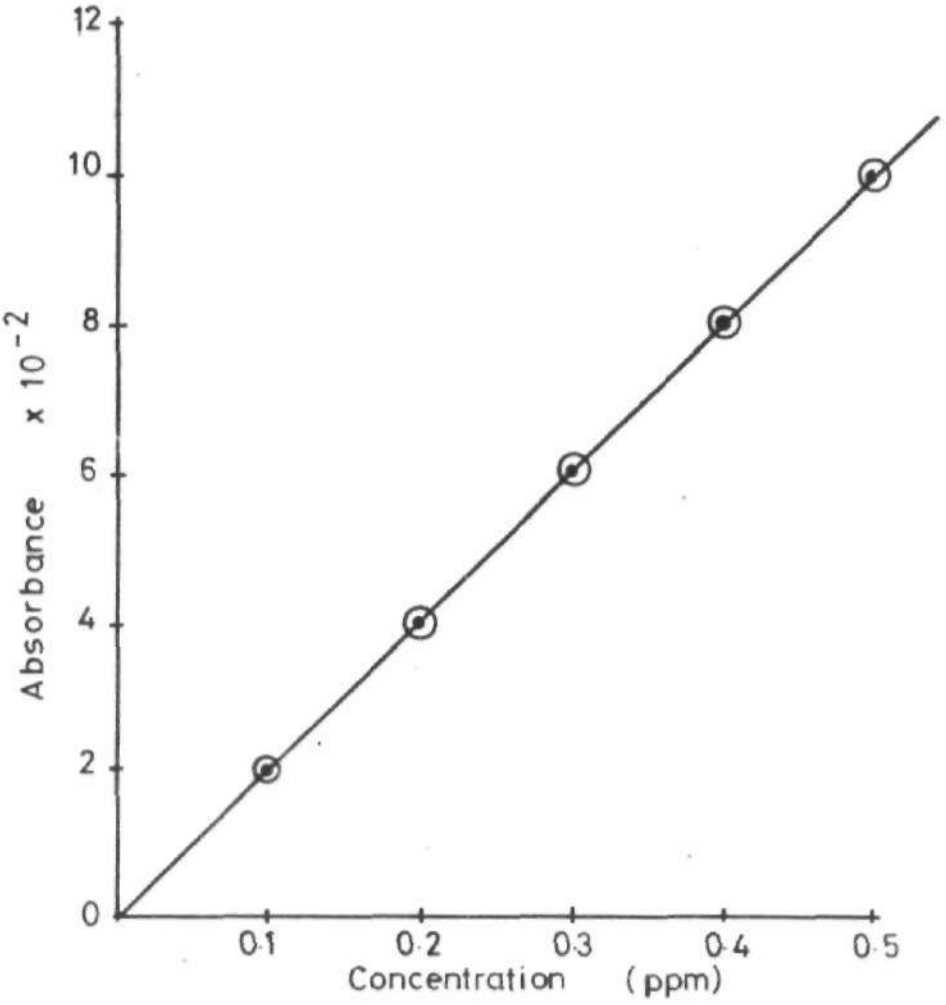


Fig. 2·1 Calibration Curve for the determination of Fluoride

2.26 Determination Of Iodine (64, 65, 66)

A number of methods are available for the determination of iodine (65). Very few are applicable in water analysis. In the ongoing discussion, the catalytic reduction (photometric) method is used. This reaction depends on the ability of the iodide ion to catalyse the reaction between yellow cerium (IV) and arsenic(III) under controlled conditions of time, temperature and acidity. The reaction

$$\underset{\text{orange}}{2Ce(IV)} + \underset{\text{colour-less}}{As(III)} \rightleftharpoons \underset{\text{colour-less}}{2Ce(III)} + \underset{\text{colour-less}}{As(V)} \quad .. \quad .. \quad (1)$$

requires many hours to reach completion without the aid of heat or a catalyst inspite of the fact that the difference of potential seems to favour spontaneous reaction. In the presence of iodine, the rate of decrease of colour increases in proportion to the amount of iodide present.

Due to the long time required for the reaction to reach completion, the reaction is stopped after a fixed time (15 minutes) by the addition of iron (II) which results in the formation of iron (III). The amount of iron (III) formed is directly proportional to the remaining cerium (IV) ions concentration. The amount of iron(III) is determined by adding potassium thiocyanate and measuring the colour intensity of the relatively stable complex formed at 525nm.

$$Fe(II) + Ce(IV) \rightleftharpoons Ce(III) + Fe(III) \quad .. \quad .. \quad (2)$$

This method has the advantages of requiring only small water samples, eliminating distillation procedures, minimising

certain interferences and giving stable colours for spectrophotometric determinations.

An excess of sodium chloride is added to attain a stable maximum chloride concentration thereby eliminating the interference of chloride already present in the water and reducing the formation of non-catalytic forms of iodine (iodate). It also overcomes the inhibitory effects of silver and mercury when present. A possible mechanism for the regeneration of the iodide catalyst is shown below:

$$Ce(IV) + I^- \longrightarrow I + Ce(III) \quad .. \quad .. \quad .. \quad (3)$$

$$2I \longrightarrow I_2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

$$I_2 + H_2O \longrightarrow HOI + I^- \quad .. \quad .. \quad .. \quad (5)$$

$$H_3AsO_3 + HOI \longrightarrow H_3AsO_4 + H^+ + I^- \quad .. \quad .. \quad (6)$$

The arsenious acid is assumed to be present in excess thereby making reaction (1) a first order reaction.

Experimental

Apparatus: (1) A waterbath capable of temperature control to 30 $\pm$ 0.5°C.

(2) A spectrophotometer for use at 525nm and providing a light path of 1cm.

(3) Fifteen 50ml volumetric flasks.

(4) A stopwatch.

Reagents: The following stock solutions were stored in tightly stoppered containers in a dark place. All chemicals were of analytical reagent grade unless otherwise stated.

(1) Deionised distilled water was used for the preparation of all reagents and as dilution water.

(2) Sodium chloride solution: Prepared by dissolving 200.0g sodium chloride in water and diluting to 1 litre.

(3) Arsenious acid (0.025M): Prepared by dissolving 4.946g arsenious oxide in water containing 4.0g potassium hydroxide and diluting to 1 litre.

(4) Ceric ammonium sulphate (0.02M): Prepared by dissolving 13.38g ceric ammonium sulphate, $2Ce(NH_4)_4(SO_4)_4 \cdot 4H_2O7$, in water containing 44ml concentrated sulphuric acid and diluting to 1 litre with water.

(5) Concentrated sulphuric acid.

(6) Ferrous ammonium sulphate reagent: Prepared by dissolving 1.5g ferrous ammonium sulphate, $2Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O7$ in 100ml of water containing 0.6ml concentrated sulphuric acid. The solution was prepared afresh during subsequent determinations.

(7) Potassium thiocyanate solution: Prepared by dissolving 40.0g potassium thiocyanate, KCSN, in water and diluting to 1 litre.

(8) Stock iodide solution: Prepared by dissolving 261.6mg anhydrous potassium iodide in water and diluting to 1 litre with

more water. (1.0ml = 200ugI i.e. 200ppm stock solution).

(9) Intermediate iodide solution: Prepared by diluting 20ml stock iodide solution to 1 litre with water. (1.0ml = 4.0ugI i.e. 4ppm intermediate iodide solution).

(10) Standard iodide solution: Prepared by diluting 25ml intermediate iodide solution to 1 litre with water. (1.0ml = 0.1ugI i.e. 0.1ppm solution of iodide).

Procedure: (a) Sample size: 10ml of each sample was used in the determination. This volume was pipetted into a 50ml volumetric flask.

(b) Colour development: Reagents were then added to each sample in the following order: 1ml sodium chloride solution, 0.5ml arsenious acid solution and 0.5ml concentrated sulphuric acid. The reaction mixtures and the ceric ammonium sulphate solution were placed in a 30°C waterbath and allowed to come to temperature equilibrium. 1ml of ceric ammonium sulphate solution was added to the flask containing water sample number one and the content of the flask mixed by inversion. A stopwatch was started to time the reaction. After 15 $\pm$ 0.1 minutes, the sample was removed from the water-bath and immediately 1.0ml ferrous ammonium sulphate reagent was added with mixing. The yellow colour of the ceric ion disappeared. 1.0ml potassium thiocyanate solution was then added with mixing. The sample was replaced in the waterbath and within 1 hour after the thiocyanate addition, the red colour was read as percent transmittance in the spectrophotometer. Several samples were run at the same time. The

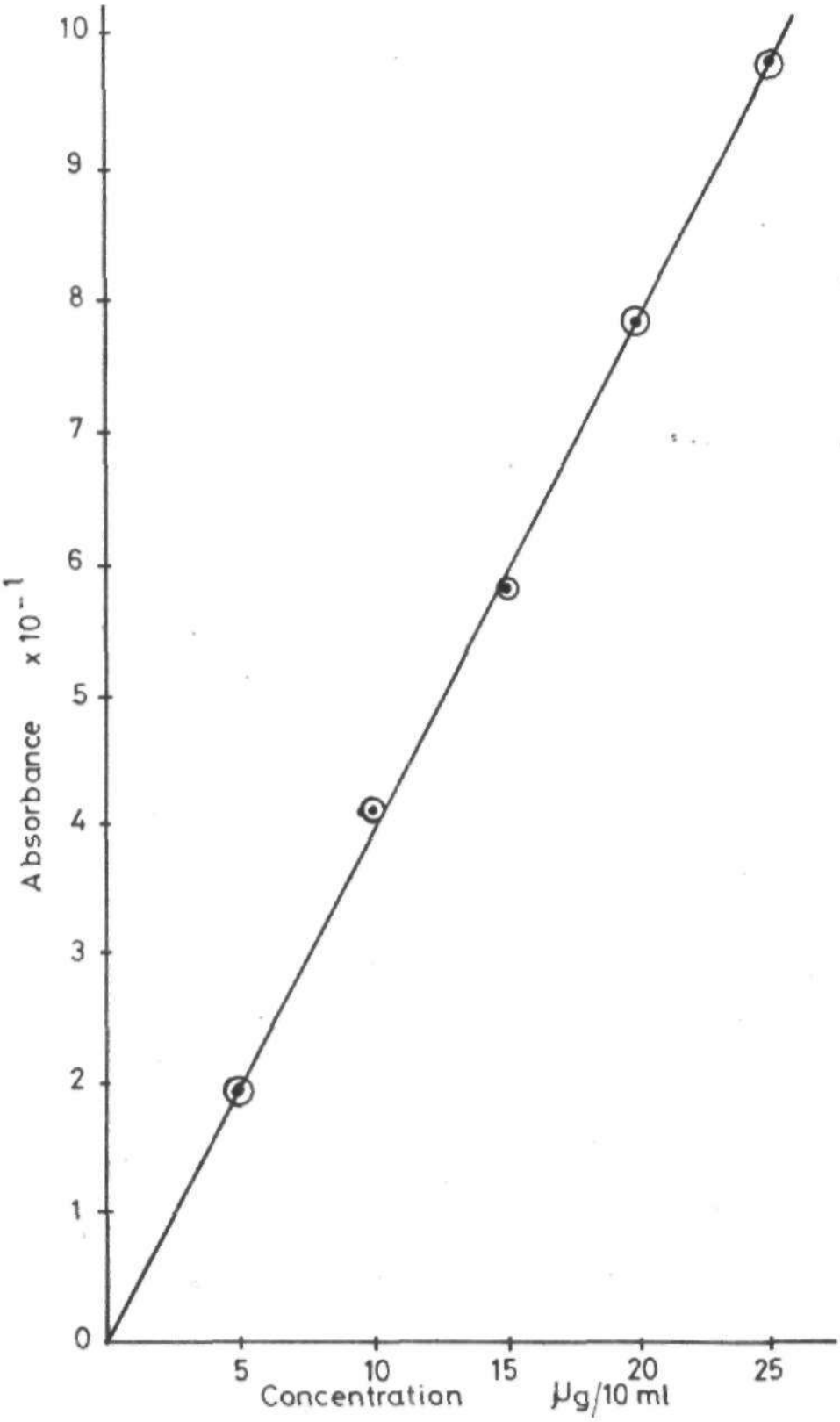


Fig 2.2 Calibration Curve for the determination of Iodine

reactions, starting from the addition of ceric ammonium sulphate, were started at 1 minute intervals to allow time for additions of ferrous ammonium sulphate and thiocyanate. Results were read from the calibration curve. Duplicate determinations were carried out for each sample and the detailed results are shown in Appendix III(h) while the summarised forms are included in Tables 3.1 to 3.4.

(c) Calibration standards: Standards containing 0, 5, 10, 15, 20, 25ugI/10ml of solution were treated as above and a calibration curve, Figure 2.2, was established. The calibration curve was checked on subsequent analyses.

Calculation: The following relationship was used:

$$\text{mg/l I} = \frac{\text{ugI determined photometrically}}{\text{ml sample}}$$

2.27 Determination of Metal Ions By Flame Photometry And Atomic Absorption Spectroscopy (67-72)

2.271 Determination of sodium and potassium using the flame photometer.

2.2711 Principle of flame photometry: Some metal ions (mostly those of groups I and II of the Periodic Table) have low ionisation potentials and therefore can ionise at low temperatures. This property is utilised in the flame photometric determination of these metals.

In this technique, the solution of the metal ion to be determined is aspirated into the flame. The solution is evaporated leaving fine salt particles suspended in the flame. The particles are then vapourised and the vapour is dissociated

into atoms. Many of the atoms are then ionised by electron loss (absorption process):

$$M \rightleftharpoons M^{+} + e^{-}$$

The degree of ionisation is however concentration dependent and increases with increase in flame temperature and a decrease in ionisation potential of the element concerned. The temperature however should not be too high so as to avoid excessive ionisation. The ionised atoms on reverting to the ground state emit radiation in the form of electromagnetic radiation and this is detected and recorded (emission process). The wavelength of the emitted radiation is governed by the energy change involved in the transition. For each element, there are certain permitted shifts giving rise to a series of lines, each series being characteristic of the element. The intensity of any one line is governed principally by the flame temperature, number of atoms of the element at any one instant and the presence of other atomic species.

The location of the lines provides qualitative information, their intensity permits quantitative analysis from the relationship:

$$I \propto C$$

where I = the radiation intensity

and C = the concentration of the determinant.

A calibration curve of intensity versus concentration is usually prepared with standard solutions of a known element. From the curve, the concentration of the analyte is found out.

2.2712 Preparation of calibration curves and samples analyses: Calibration curves for sodium and potassium were prepared as detailed below. Samples were analysed by direct aspiration into the flame and readings were interpolated to the curve to get the corresponding concentrations in the sample. Duplicate determinations were carried out for each sample. Summaries of the results are included in Tables 3.1 to 3.4 while detailed results of weekly analyses are shown in Appendices III(i) and III(j) for sodium and potassium respectively. On subsequent analyses, the highest concentration of each (5ppm for sodium and 10ppm for potassium) was used to set the instrument at 100% intensity.

Experimental

Apparatus: (1) A flame photometer, corning EEL scientific instruments, Evans Electroselenium Ltd., England.

(2) Twenty 100ml volumetric flasks.

Reagents: (1) Deionised distilled water was used for the preparation of all reagents and as dilution water.

(2) Sodium chloride solution.

(3) Potassium chloride solution.

All chemicals were of analytical reagent grade. Details of the preparation of the solutions are given below under procedure.

Procedure: (a) Sodium: A 1000ppm stock solution of sodium was prepared by dissolving 2.542g sodium chloride (dried

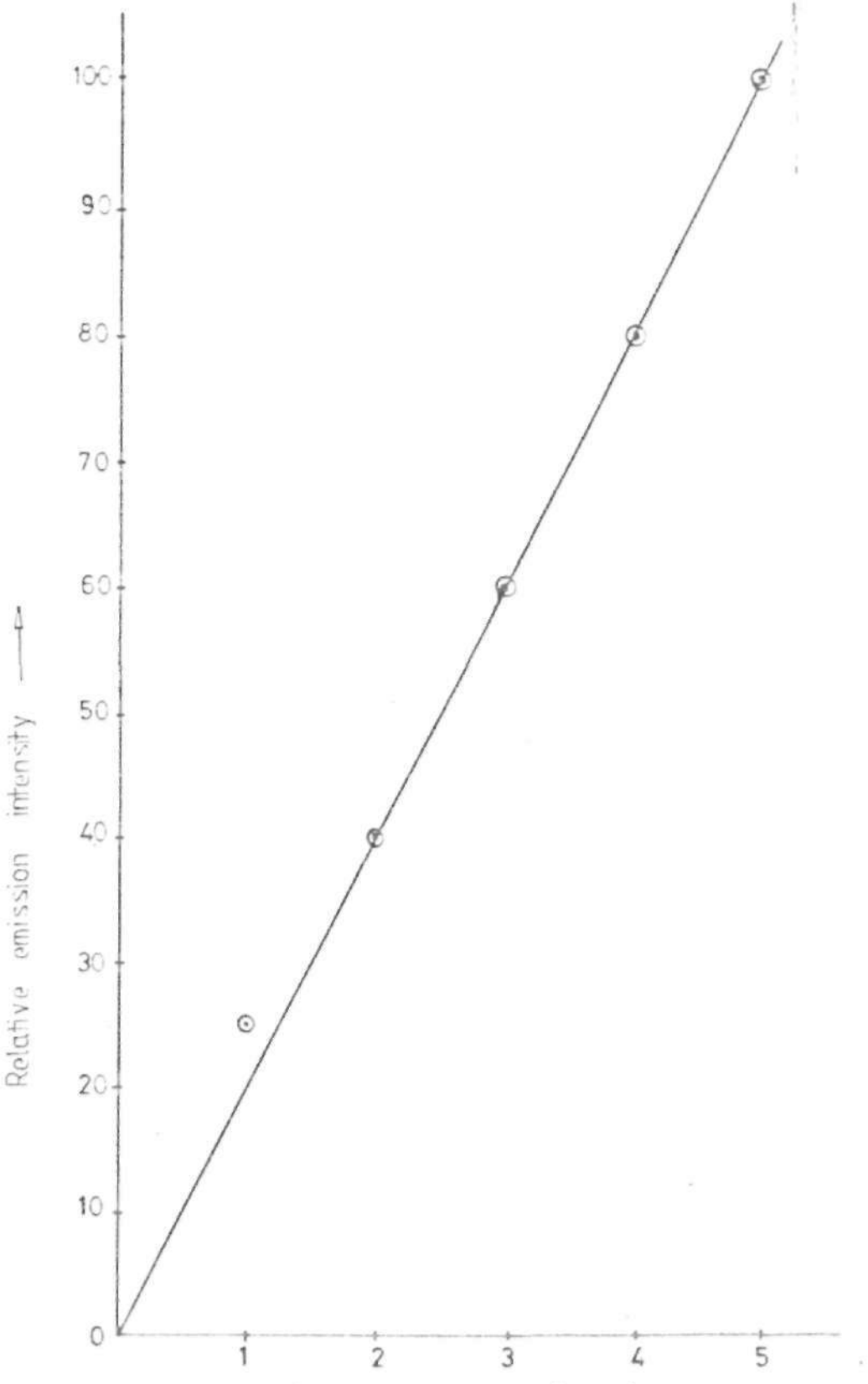


Fig 2.3 Calibration Curve for the determination of Sodium

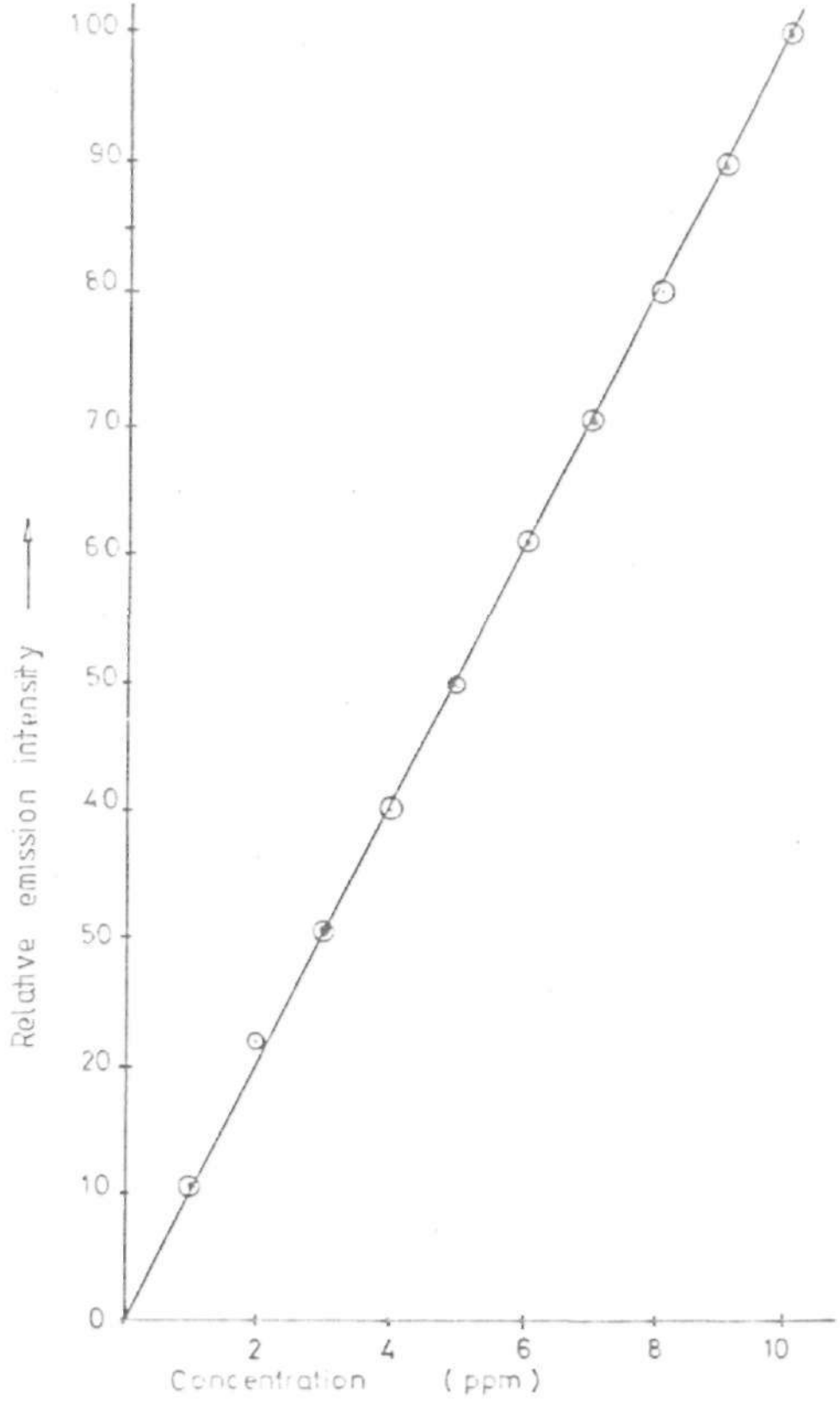


Fig.2 4 Calibration Curve for the determination of Potassium

at 140°C for 1 hour and cooled in a desiccator) in a small quantity of water and then diluted to 1 litre with more water From this stock, 10ml aliquot was diluted to 100ml to give an intermediate solution containing 100ppm sodium. From this intermediate, 1 to 5ppm standard solution of sodium in 100ml were prepared by appropriate dilutions with water. The calibration curve is shown in Figure 2.3.

(b) Potassium: A stock solution containing 1000ppm potassium was prepared by dissolving 1.907g potassium chloride (dried at 110°C) in a small quantity of water and diluting to 1 litre with more water. An intermediate potassium solution was prepared by diluting 10ml stock solution to 100ml with water to give a solution containing 100pm. From this, 1ppm to 10ppm potassium solutions in 100ml were prepared by diluting appropriate volumes with water. The calibration curve is shown in Figure 2.4.

2.272 Determination of Calcium, Magnesium, Iron, Zinc, Copper, Manganese, Lead, Arsenic and Mercury Using The Atomic Absorption Spectrophotometer

2.2721 Principle of atomic absorption spectroscopy: The technique involves the absorption of energy by atoms that are in their ground states. It is based on the fact that metal atoms absorb radiation strongly at discrete characteristic wavelengths that coincide with the emission spectral lines of the particular metal. The sample solution is aspirated into the flame and the element is converted into its atomic vapour state. Most of the atoms in the flame remain in their ground (unexited) states and this technique measures the ground state

atoms. An external source supplies a beam of light which traverses the flame and is focused on the entrance slit of a monochromator that has been set to read the intensity of the chosen spectral line. Light with this wavelength is then absorbed by the metal in the flame and the degree of absorption is a function of the concentration of the metal in the flame. The light source is usually choppered to eliminate the interference of emitted light from the flame.

To determine the concentration of a particular metal in an unknown sample, a calibration curve of concentration versus absorbance is usually prepared using standard solutions of varying concentrations of the metal ion. From such a curve, the quantity of the metal ion present in the unknown is usually found out.

As with flame emission, the location of the absorption lines serves to identify the components of a sample; the absorbance of a line as in solution spectrometry is generally proportional to the concentration of the absorbing species.

2.2722 Preparation of calibration curves and samples analyses: Calibration curves for calcium, magnesium, iron, zinc, copper, manganese, lead, arsenic and mercury were prepared as detailed below. Duplicate determinations were carried out for each sample and the average was used. The results are summarised in Tables 3.1 to 3.4 while details are given in Appendices III(k) to III(o). The calibration curves were checked during subsequent analyses. The calibration curves for these metals are shown in Figures 2.5 to 2.9. Calibration

curves for metals which were absent in the samples are not included.

Experimental

Apparatus: (1) A Unicam SP1900 Atomic Absorption Spectrophotometer equipped with a standard air-acetylene burner head and individual hollow cathode lamps of the elements investigated.

(2) Thirty-five 100ml volumetric flasks.

Reagents: All chemicals were of analytical reagent grade.

(1) Deionised distilled water was used for the preparation of all reagents and as dilution water.

(2) Calcium solution: Prepared by dissolving 630mg calcium carbonate in 10ml concentrated hydrochloric acid and diluting to 1 litre with water. A stock solution of 3 litres was prepared for use throughout the period of analysis.

(3) Lanthanum solution, 1% m/V: Prepared by dissolving 3.1175g Lanthanum nitrate in water and diluting to 1 litre with more water. A stock solution of 3 litres was prepared for use throughout the period of analysis.

(4) Standard solutions of the metal ions as detailed under procedure.

Procedure: (a) Calcium: A 1000ppm calcium stock solution was prepared by adding 2.4970g calcium carbonate to about 50ml of water. Concentrated hydrochloric acid was then added

dropwise to effect complete disolution. The resulting solution was then diluted to 1 litre with water. The solution was standardised with 0.1M EDTA solution using Eriochrome Black T as indicator (73). 1ml of the stock calcium solution was diluted to 100ml with water to give a solution of 10ppm calcium. 1 to 5ppm standard calcium solutions in 10ml were prepared by appropriate dilutions of the 10ppm solution with water. The 10ml of each standard solution was mixed with 2.5ml lanthanum solution before aspirating. Sample solutions were diluted but similarly treated.

(b) Magnesium: A 1000ppm stock magnesium solution was prepared by dissolving 10.0135g magnesium sulphate heptahydrate, $MgSO_4.7H_2O$, in about 200ml water. 1.5ml concentrated nitric acid was added and the volume made up to 1 litre with water. The solution was standardised with 0.1M EDTA solution using Eriochrome Black T as indicator (73). An intermediate 10ppm magnesium solution was prepared by diluting 1ml aliquot of the stock solution to 100ml. A 0.1 to 1.0ppm standard solutions of magnesium in 10ml were prepared by appropriate dilutions of the intermediate solution with water. 10ml of each standard solution was mixed with 2.5ml lanthanum solution before aspirating. Sample solutions were diluted but similarly treated.

(c) Iron: A 1000ppm solution of iron(II) was prepared by dissolving 4.9778g ferrous sulphate heptahydrate,

$FeSO_4.7H_2O$, in water containing 50ml concentrated sulphuric acid and the volume made to 1 litre with water. The solution was standardised with 0.01M potassium dichromate solution using N-phenylanthranilic acid as indicator (73). An intermediate 10ppm iron(II) solution was prepared by diluting 1ml stock solution to 100ml with water. From this, 1 to 5ppm iron(II) standard solutions in 10ml were prepared by appropriate dilutions with water. 10ml of each standard was mixed with 2.5ml calcium ion solution before aspirating. Samples were similarly treated.

(d) Zinc: A 1000ppm stock solution of zinc was prepared by dissolving 4.3980g zinc sulphate heptahydrate, $ZnSO_4.7H_2O$, in water and the volume made to 1 litre with more water. The solution was standardised with 0.1M EDTA solution using Eriochrome Black T as indicator (73). An intermediate 10ppm zinc solution was prepared by diluting 1ml stock solution to 100ml with water. 1 to 5ppm zinc solutions were prepared in 10ml by appropriate dilutions of the intermediate with water. Samples were aspirated directly into the flame.

(e) Copper: A 1000ppm stock copper solution was prepared by dissolving 3.7980g copper nitrate trihydrate, $Cu(NO_3)_2.3H_2O$, in a small quantity of water and the volume made up to 1 litre with more water. The solution was standardised with 0.1M sodium thiosulphate solution using starch as indicator (73). An intermediate 10ppm copper solution was prepared by diluting 1ml of the stock solution to 100ml with water. From this intermediate solution, 1 to 5ppm standard copper solutions in 10ml were prepared by appropriate dilutions

with water. Standard addition method was used for sample analysis.

(f) Lead: A 1000ppm stock solution was prepared by dissolving 1.5984g lead nitrate in a small quantity of water and the volume made up to 1 litre with more water. The solution was standardised with 0.1M EDTA solution using xylenol orange as indicator (73). An intermediate 10ppm lead solution was prepared by diluting 1ml lead stock solution to 100ml with water. From this, 1 to 5ppm lead standard solutions in 10ml were prepared by appropriate dilutions of the intermediate with water. Standard addition method was used for the analyses of the samples.

(g) Manganese: A 1000ppm manganese solution was prepared by dissolving 4.060g manganous sulphate heptahydrate in a small quantity of water containing 1.5ml concentrated nitric acid and the volume made up to 1 litre with water. The solution was standardised with 0.1M EDTA solution using Eriochrome Black T as indicator (73). An intermediate 10ppm manganese solution was prepared by diluting 1ml stock solution to 100ml with water. 1 to 5ppm standard manganese solutions in 10ml were then prepared by appropriate dilutions of the intermediate solution with water. Standard addition method was used for the analysis of the samples. Each 10ml of solution was mixed with 2.5ml of calcium solution before aspirating.

(h) Mercury: A 1000ppm stock solution of mercury was prepared by dissolving 1.3520g mercury(II) chloride, $HgCl_2$, in

250ml deionised water and then diluted with more water to 1 litre and stored in a polythene bottle. The solution was standardised with 0.1M potassium iodate (73). From this stock, 1 to 5ppm standard solutions in 100ml were prepared by appropriate dilutions.

(i) Arsenic: A 1000ppm stock solution of arsenic was prepared by dissolving 1.3200g arsenic trioxide, As_2O_3, in 50ml hydrochloric acid (S.G. 1.18) and diluted to 1 litre in a volumetric flask with water. The solution was standardised with 0.1M potassium iodate (73). From this stock solution, 1 to 5ppm standard solutions in 100ml were prepared by appropriate dilutions.

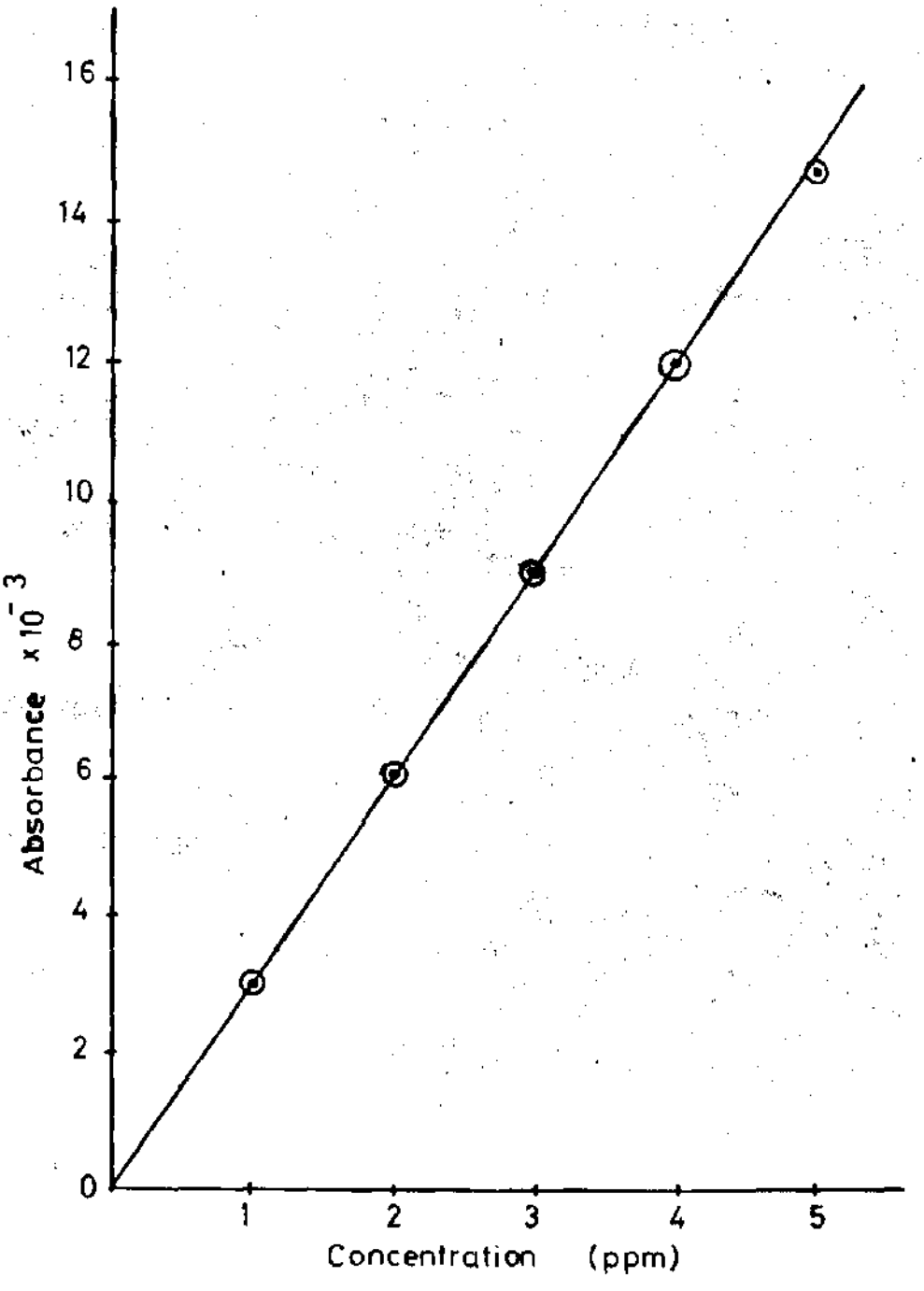


Fig. 2.5 Calibration Curve for the determination of Calcium

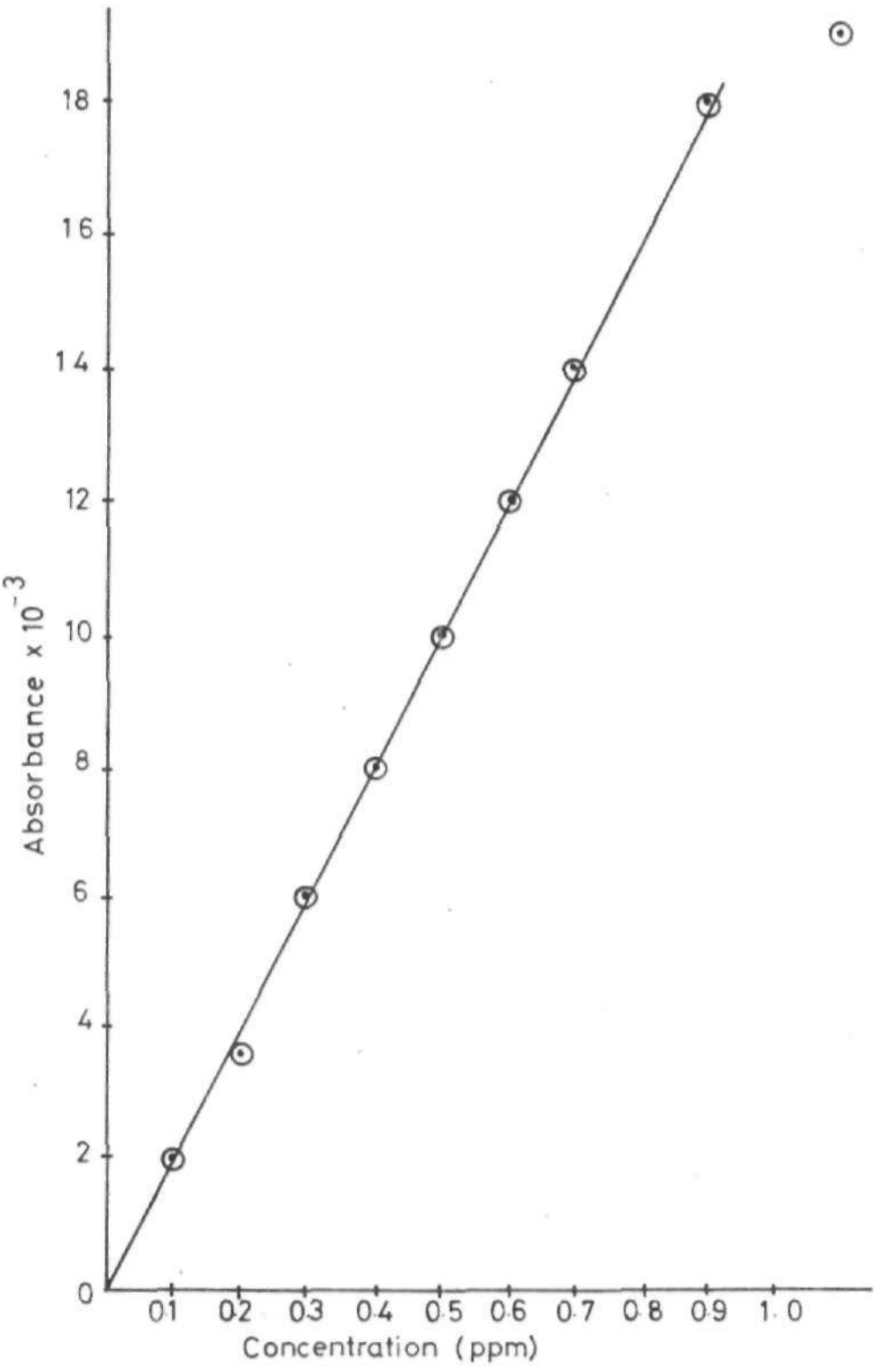


Fig 2·6 Calibration Curve for the determination of Magnesium

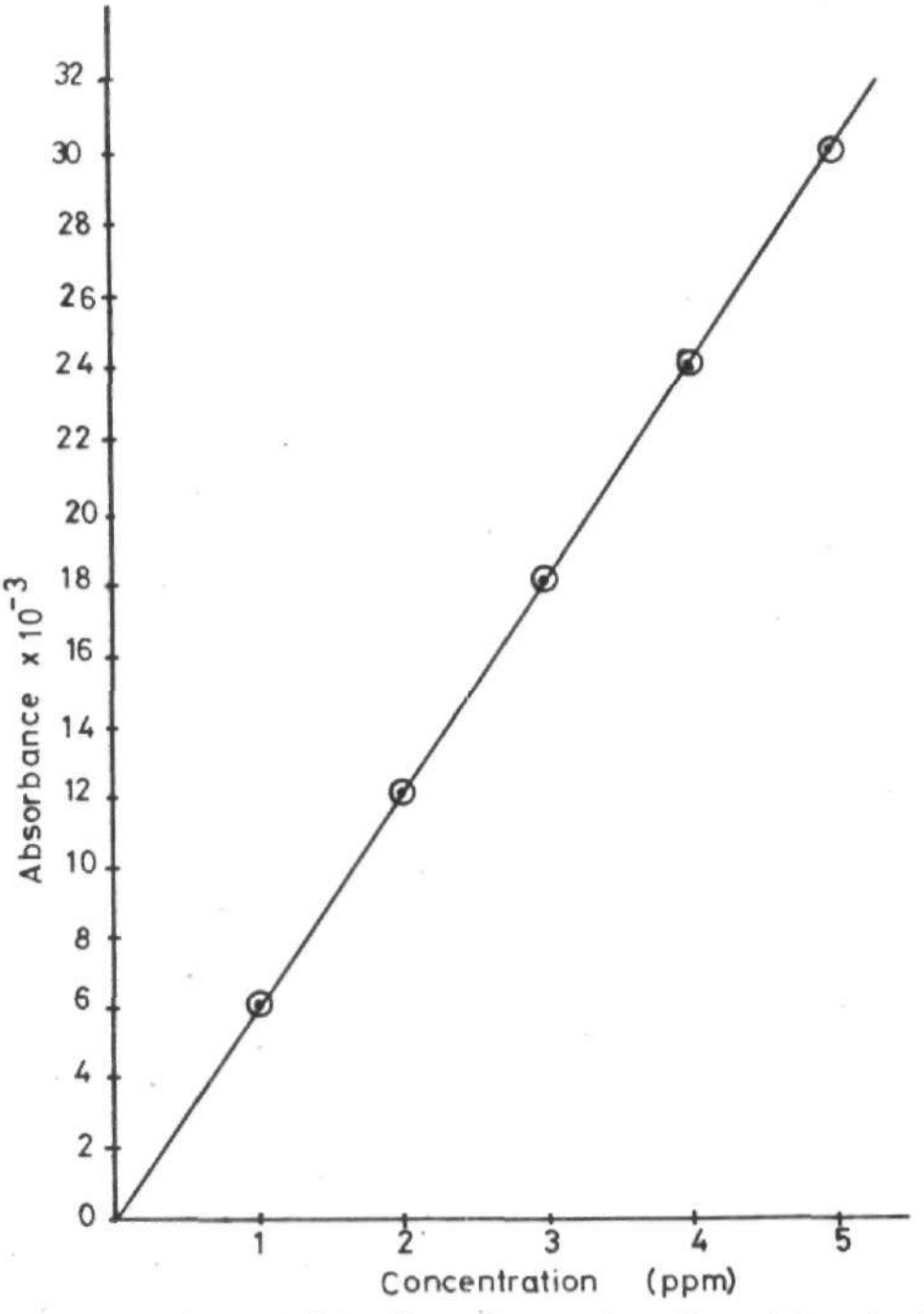


Fig 2.7 Calibration Curve for the determination of Iron

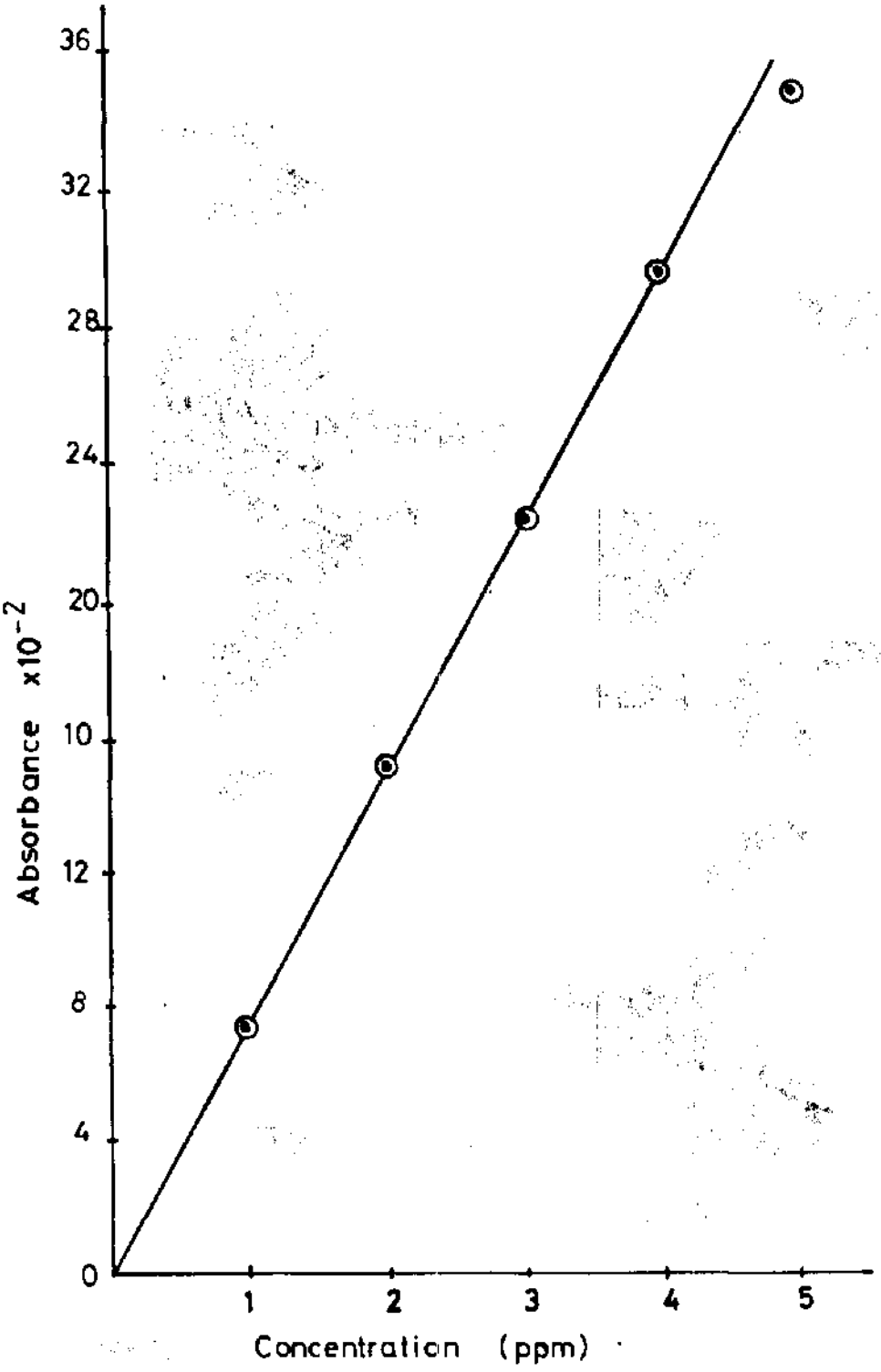


Fig. 2·8 Calibration Curve for the determination of Zinc

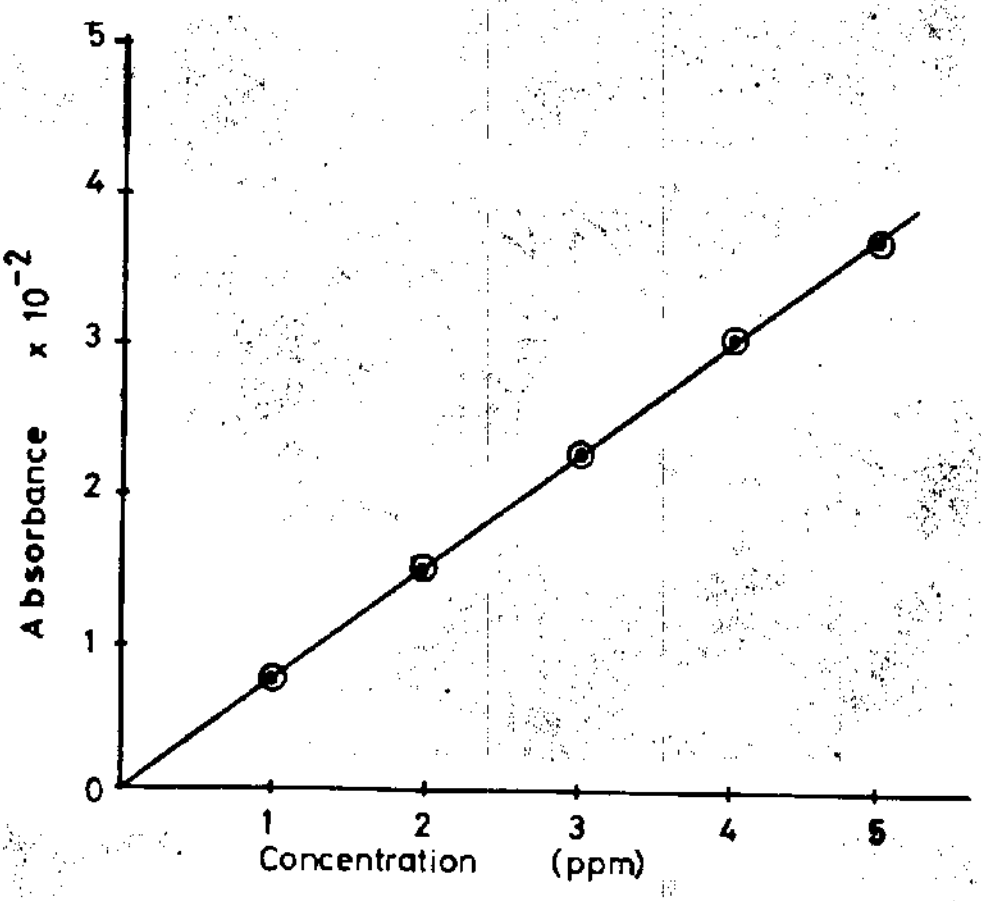


Fig. 2.9 Calibration Curve for the Determination of Lead

CHAPTER 3

RESULTS AND DISCUSSION

3.1 RESULTS

Detailed results of the complete analysis are shown in the Appendix. The average values indicate such amounts of the particular constituents as ingested by continuously consuming water from the same sampling point throughout the period of analysis. These average values were calculated from the values obtained from the ten collections for each sample. The results are summarised in the following Tables which indicate the maximum, median and minimum values of each determinant throughout the period of investigation. In the formation of the Tables, the raw water from the Zaria waterworks, the treated water collected from the different points within Zaria, the treated water from the Ahmadu Bello University waterworks and the raw water from the Ahmadu Bello University dam are considered separately.

Table 3.1

Range In Quality Of Treated Water Collected From The Different Sampling Points Within Zaria

Constituent Or Property	Unit Of Expression	Maximum	Median	Minimum
pH	pH units	9.2	7.9	6.2
Conductivity at 25°C	μscm^{-1}	110.0	94.0	75.0
Total solids	ppm	112.0	86.5	64.0
Filtrable residue	"	89.0	77.0	63.0
Non-filtrable residue	"	34.0	8.0	1.0
Fluoride (F)	"	4.0	2.0	1.0
Chloride (Cl)	"	18.5	10.0	5.5
Iodide (I)	"	0.65	0.154	0.0
Sodium (Na)	"	5.0	4.3	2.2
Potassium (K)	"	5.6	4.8	4.1
Calcium (Ca)	"	15.0	4.8	1.2
Magnesium (Mg)	"	5.0	2.45	0.90
Iron (Fe)	"	1.75	0.70	0.17
Zinc (Zn)	"	2.06	0.09	0.03
Copper (Cu)	"	0.0	0.0	0.0
Lead (Pb)	"	0.5	0.0	0.0
Manganese (Mn)	"	0.0	0.0	0.0
Arsenic (As)	"	0.0	0.0	0.0
Mercury (Hg)	"	0.0	0.0	0.0

Table 3.2

Range In Quality Of Raw Water From The Zaria Dam

Constituent Or Property	Unit of Expression	Maximum	Median	Minimum
pH	pH units	7.8	7.45	6.8
Conductivity at 25°C	μscm^{-1}	67.0	62.75	45.0
Total solids	ppm	150.0	99.0	88.0
Filtrable residue	"	139.0	87.0	82.0
Non-filtrable residue	"	15.0	10.0	4.0
Fluoride (F)	"	3.0	2.0	1.0
Chloride (Cl)	"	9.4	6.4	5.0
Iodide (I)	"	0.45	0.076	0.0
Sodium (Na)	"	4.8	4.5	3.1
Potassium (K)	"	5.5	5.2	4.6
Calcium (Ca)	"	5.3	3.15	2.0
Magnesium (Mg)	"	5.0	2.78	0.9
Iron (Fe)	"	4.75	1.10	0.5
Zinc (Zn)	"	2.19	0.10	0.05
Copper (Cu)	"	0.0	0.0	0.0
Lead (Pb)	"	0.5	0.10	0.0
Manganese (Mn)	"	0.0	0.0	0.0
Arsenic (As)	"	0.0	0.0	0.0
Mercury (Hg)	"	0.0	0.0	0.0

Table 3.3

Range In Quality Of Treated Water From A.B.U. Waterworks

Constituent Or Property	Unit of Expression	Maximum	Median	Minimum
pH	pH units	10.0	9.3	8.8
Conductivity at 25°C	μscm^{-1}	114.0	102.0	92.5
Total solids	ppm	119.0	91.5	83.0
Filtrable residue	"	95.0	83.0	75.0
Non-filtrable residue	"	24.0	8.0	4.0
Fluoride (F)	"	3.0	2.0	1.0
Chloride (Cl)	"	20.0	10.0	8.5
Iodide (I)	"	0.35	0.16	0.0
Sodium (Na)	"	4.7	4.35	2.7
Potassium (K)	"	6.2	4.9	4.6
Calcium (Ca)	"	17.9	4.35	3.3
Magnesium (Mg)	"	3.0	2.0	0.77
Iron (Fe)	"	2.22	0.63	0.26
Zinc (Zn)	"	2.16	0.55	0.15
Copper (Cu)	"	0.0	0.0	0.0
Lead (Pb)	"	0.1	0.0	0.0
Manganese (Mn)	"	0.0	0.0	0.0
Arsenic (As)	"	0.0	0.0	0.0
Mercury (Hg)	"	0.0	0.0	0.0

Table 3.4

Range In Quality Of Raw Water From The ABU Dam

Constituent Or Property	Unit of Expression	Maximum	Median	Minimum
pH	pH units	7.9	7.8	6.9
Conductivity at 25°C	μscm^{-1}	73.0	70.5	64.8
Total solids	ppm	407.0	305.0	267.0
Filtrable residue	"	381.0	295.0	256.0
Non-filtrable residue	"	26.0	17.5	3.0
Fluoride (F)	"	8.0	6.5	4.0
Chloride (Cl)	"	7.2	5.0	4.0
Iodide (I)	"	0.215	0.082	0.03
Sodium (Na)	"	4.6	4.0	3.4
Potassium (K)	"	9.1	8.15	7.1
Calcium (Ca)	"	8.2	2.7	1.4
Magnesium (Mg)	"	4.5	2.7	1.0
Iron (Fe)	"	2.87	0.63	0.2
Zinc (Zn)	"	1.79	0.09	0.03
Copper (Cu)	"	0.0	0.0	0.0
Lead (Pb)	"	0.5	0.3	0.0
Manganese (Mn)	"	0.0	0.0	0.0
Arsenic (As)	"	0.0	0.0	0.0
Mercury (Hg)	"	0.0	0.0	0.0

3.2 DISCUSSION

In the section captioned "chemical treatment of water for public supply", it has already been mentioned that the concentrations of the chemicals added to water during treatment vary from day to day. It is not therefore unexpected that the concentrations of some of such substances remaining in the water after treatment vary accordingly from day to day. Another point worth mentioning is that since most of the determinants come into water through tank and piping materials, the concentration of such substances is a function of the period of contact of the water with the tank and pipe. This explains why in some cases, the concentration of some of the determinants as shown in the Tables are higher in the treated water than in the raw samples. Inspite of the above limitations, however, meaningful results were obtained.

It is also pertinent to mention here that the raw water samples from the Zaria and ABU dams are so turbid that they are not actually used for drinking and most other domestic purposes. These two sources were included in the research work in order to observe the variation that occurs in determinant concentrations in both the treated and raw water samples.

Though it has been stated (74) that treatment is not likely to alter the concentrations of magnesium, fluoride, aluminium, zinc, copper, lead, nitrite, nitrate, chloride that were present in the original raw water, one cannot confidently conclude, for there must be a change in concentration of these substances as the water passes through tank and piping materials,

instrumental conditions apart, thereby leading to changes in these parameters in the treated samples and hence making it difficult to correlate. The ongoing discussion is divided into parts, each part dealing with one or more parameters determined. The quality standards stipulated by the WHO (75, 76) at different periods are given in Appendices I and II.

3.21 pH

The pH of the samples analysed range from 6.2 to 9.2 with a median value of 7.9 for the treated water samples collected from the different points within Zaria; 6.8 to 7.8 with a median value of 7.45 for the raw water from the Zaria dam; 8.8 to 10.0 with a median value of 9.3 for the treated water from the ABU waterworks and 6.9 to 7.9 with a median value of 7.8 for the raw water from the ABU dam. In almost all cases, the treated water from the ABU waterworks has the highest pH value. This corresponds to the high calcium content the water is found to contain. However, these high values are only slightly above the WHO highest desirable level of 9.2.

3.22 Conductivity

The treated water samples from Zaria have conductivities in the range 75.0 to 110.0 with a median of 94.0 while the treated water from the ABU waterworks has conductivity values in the range 92.5 to 114.0 with a median of 102.0. The raw water samples from Zaria dam have values in the range 45.0 to 67.0 with a median of 62.75 while those from the ABU dam range between 64.8 to 73.0 with a median of 70.5. All conductivity values recorded for the raw water samples from both sources are lower than the corresponding

values for the treated samples. This is because more substances responsible for ionic conductance go into the water during treatment and in the distribution system. Generally, the conductivity values for all samples are low. This may be due to the fact that both the number and concentration of the ions in solution are low.

3.23 Residue

As should be expected, the total residue values are high for the raw water samples. The values for filtrable and non-filtrable residues however varied irregularly for the treated water samples depending mainly on the amount of sediment in the path taken by the water. The amount of coloured residue present in the raw water samples renders the water turbid and unhealthy for consumption. However, the values for both treated and raw water samples are below the WHO limit of 1500ppm. These low values are indicative of clean drinking water.

3.24 Fluoride

At both the Zaria and ABU waterworks, the water is neither specifically fluoridated nor defluoridated during treatment. The results of this analysis have shown that the ABU dam water contains a high quantity of fluoride ranging between 4.0 to 8.0ppm while that of water from the Zaria dam ranges between 1.0 and 3.0ppm. All the treated water analysed have fluoride concentrations ranging between 1.0 and 3.0ppm. The frequency with which values outside the WHO (1971) standard of 1.7ppm occured is a case for

concern and requires the attention of the water authorities. A similar high result was obtained for well waters of Nagaur and Jaipur districts in Rajasthan (77) and the waters were said to be unsuitable for drinking and even irrigation.

3.25 Iodide

Just like fluoride, iodide is neither added nor is that naturally occuring removed. Much of the values for the treated water samples are outside the BMA limit of 0.1-0.15ppm. At the early period of sample collection, the values were low. This is possibly because this was the later part of the rainy season when the iodine in the water is likely to be greatly diluted in the raw water samples. However, it is surprising that the iodine content of the raw water samples are lower than those for the treated samples. No explanation seems to be immediate.

3.26 Chloride

The WHO (1971) standard for drinking water is 600ppm. Throughout the analysis, all the values obtained in both raw and treated water samples are much lower than the stated standard though as expected, these are higher in the treated than raw water samples. However, it has been stated that provided it is not very excessive, the actual amount of chloride in drinking water is in itself a matter of very little importance for since common salt is an article we require and take, in some shape or other, everyday in our lives, it can be of very little consequence whether or not

we take some of it in the water we drink (78).

3.27 Sodium And Potassium

There are no standards from the WHO for comparison. The values obtained for sodium and potassium in this work are low considering the geographical features of this area where the raw water samples originate. The values do not even compare with those got in the public water supplies of the 100 largest cities in the United States; the values being 198ppm (maximum), 12ppm (median), 1.1ppm (minimum) (79). However, the levels of potassium are generally higher than those of sodium throughout the analysis though potassium has no significance in public water supplies or in water used for industrial purposes.

3.28 Calcium And Magnesium

The values obtained for calcium in the raw water samples are generally lower than in the treated samples. The reason is quite obvious. Calcium oxide is added to water during treatment to regulate the pH of the water. For the first two and tenth collections, the values were higher than those obtained for other collections. There is a wide variation in the values obtained for the samples during a particular collection. This variation in the calcium ion concentration may be due to variations in the amount of calcium oxide added to the water during each treatment. Since the treated water passess into a reservoir and later pumped into tanks, there is a high degree of mixing depending on the amount of water already in each tank and the rate at

which it flows out. However, the calcium requirement of the human body is so high and the values obtained in this analysis do not compare with the WHO standard value (1971) of 200ppm.

Values obtained for magnesium were low at the initial stage of the work. The results obtained for the raw water samples compared favourably with those for the treated samples but in all cases, they are lower than the WHO (1971) standard of 150ppm. The obtained values for calcium and magnesium are too small if the calcium and magnesium in the water are to act as protectives against the development of fluorosis.

3.29 Iron And Zinc

These are ions which enter treated water mainly from the tank and piping materials. At the initial stage of the analysis, the values obtained for both elements were high. At the later stage of this work, there was severe drought in Zaria and the period of contact of the water with the distribution materials was short. Thus, much of these ions was not expected to dissolve in the water from the Zaria waterworks. The values obtained in the analysis for the raw water samples were in most cases higher than those for the treated water for iron and comparable in most cases for zinc. In all cases however, they compared favourably with the WHO standards of 1.0ppm for iron and 5.0ppm for zinc. However, water from the ABU waterworks is not very much used by the university community except during scarcity

of water supply from the Zaria waterworks. The water therefore remains stagnant in the tank and pipe for a long time. This accounts for the increase in concentration observed for zinc in the ABU waterworks treated water.

3.210 Copper

Copper has been found to be absent in the samples throughout the analysis. This is confirmed by the result of an earlier worker (80) who included a tap water sample in her analysis of some industrial effluents. However, the presence of dissolved copper in drinking water depends on the amount of copper the water can dissolve, the material composition and the copper tube defects; a high concentration of dissolved oxygen and a low bicarbonate increases copper solubility (81). However, these latter parameters were not determined in this work to be able to ascertain their influence on the absence of copper in the water. Little or no copper in a water makes the sample good for drinking since the WHO excessive limit (1958) and recommended value (1971) is 1.5ppm. But, copper is an essential element for plants and animals, it is a component of several enzymes that perform important biological functions.

3.211 Manganese And Lead

Throughout the period of analysis, manganese has been found to be absent in both the raw and treated water samples. Even if manganese were to be present in the raw water samples, chlorination could have resulted in the formation of "black slime" so that the manganese is not present in the water in

the pure form and therefore difficult to detect.

The difficulties associated with the determination of lead have already been referred to (36). Traces of the element have been detected in the raw water samples. In a very few instances, traces have also been detected in the treated samples. Where detected, the values are lower than in the raw water samples and the occurence is not enough to render the water unfit for drinking. The reason for the inability to get lead in the same amounts in both raw and treated water samples seems obvious. Lead sulphate and lead choride are salts known to be insoluble in water. It is therefore likely that the addition of aluminium sulphate may result in the precipitation of lead sulphate at the coagulation stage of treatment while chlorination may bring about the formation of lead chloride. In an area where there is much lead in the soil over which the water flows, an appreciable quantity may be expected in the raw water and perhaps in the treated samples.

3.212 Arsenic And Mercury

These metals were found to be absent in both the treated and raw water samples. This may not indicate that they are totally absent in the water but that their concentrations are beyond the detection limits by the method used. However, that there are fishes surviving in the raw water sources may indicate that these metals are either absent altogether or present in extremely trace amounts. The health effects of populations occupationally exposed to mercury and mercury compounds have long been recognised

but contamination of the general environment is of recent origin. There is no indication that concentrations of mercury in drinking water or air have contributed in any significant way to the methylmercury intoxication of the general population (82). The sensitivity for flame determination is not sufficient for determinations of mercury at the low levels required in environmental work (83).

3.3 SUMMARY AND CONCLUSIONS

This project involves ascertaining the quality of drinking water in Zaria which gets its water supply from the Zaria waterworks. Samples were collected to cover the different sections of Zaria community as per the number of distribution tanks supplying water to these areas. A raw water sample was also taken from the Zaria dam which serves as a source of raw water to the Zaria waterworks. A sample was also taken from the ABU dam and a treated sample from the ABU waterworks. These raw water samples were included in order to observe the kind of variations that occur in the concentrations of determinants between raw and treated samples. The samples were collected forthnightly in September and October and thereafter weekly up till early December, 1982.

Analysis included the determinations of pH, conductivity, residue (total, filtrable, non-filtrable), chloride, fluoride, iodide, sodium, potassium, calcium, magnesium, zinc, copper, iron, manganese, lead, arsenic, and mercury. Results were compared with WHO specified standards. Sodium

and potassium were determined by flame photometry and the other metals mentioned above by Atomic Absorption Spectrophotometry. pH, conductivity, residue, chloride, calcium, magnesium, iron, zinc, and lead have values within the WHO specified limits. Copper, manganese, arsenic and mercury were found to be absent in the samples. Iodide in a few instances has been found to be present in concentrations outside the specified limits in the treated samples. Fluoride has been found to be present in both raw and treated samples in concentrations much outside the WHO specified limits.

The results of these analyses show that there is no serious hazards in consuming the water supplied by both waterworks since most of the parameters including the toxic metals are below the standards recommended by the WHO. The attention of the water authorities must however be drawn to the high fluoride content of the water. The ABU waterworks must do something to bring the pH of their treated water within the WHO limits. However, in different parts of the world, human beings exhibit varying degrees of tolerance to these substances present in water.

3.4 SUGGESTIONS

The field of water analysis particularly drinking water, is still young in Nigeria. Much still has to be done if the public must be supplied with a good quality of water. This present work concentrated on some chemical aspects. Certain other parameters like the determinations of chromium, nitrate, cyanide, phenolic compounds and the microbiological

aspects were not included. A further research in these areas may therefore be necessary.

In order to ensure the supply of good quality water to the public, a legislation on water pollution control and sewage disposal is necessary. "The legislative aspects involved in water pollution control are very important though they tend to be overlooked in the process. Proper legislation must precede and then follow the control measures. It has to be drafted and adequately implemented in order to support and lead to a successful control" (84).

In addition to the WHO standards, the Federal Ministry of Water Resources should provide standards for both domestic and drinking water in particular here in Nigeria. This can subsequently be adopted for the African continent as a whole. Efforts should also be made to satisfy the standards required by the industries. In doing the above, the common food substances we ingest should be taken into consideration.

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APPENDIX I

Drinking Water Standards Of The World Health Organisation (74)
(concentrations are in ppm)

	(WHO International (1958))			(WHO European (1961))	
Chemical Constituent	Permissible Limit	Excessive Limit	Maximum Allowable	Recommended Limit	Tolerance Limit
Ammonia (NH_4)	-	-	-	0.5	*
Arsenic	-	-	0.2	-	0.2
Cadmium	-	-	-	-	0.05
Calcium	75	200	-	-	-
Chloride	200	600	-	350	-
Chromium (hexavalent)	-	-	0.05	-	0.05
Copper	1.0	1.5	-	3.0*	-
Cyanide	-	-	0.01	-	0.01
Fluoride	-	-	-	1.5	-
Iron	0.3	1.0	-	0.1	-
Lead	-	-	0.1	-	0.1
Magnesium	50	150	-	125+	-
Magnesium + Sodium Sulphates	500	1000	-	-	-
Manganese	0.1	0.5	-	0.1	-
Nitrate (as NO_3)	-	-	-	50	-
Oxygen, dissolved (minimum)	-	-	-	5.0	-
Phenolic compounds (as phenols)	0.001	0.002	-	0.001	-
Selenium	-	-	0.05	-	0.05
Sulphate	200	400	-	250	-
Total solids	500	1500	-	-	-
Zinc	5.0	15	-	5.0	-

*After 16 hours contact with new pipes; but water entering a distribution system should have less than 0.05ppm of copper.

+If there are 250ppm of sulphate present, magnesium should not exceed 30ppm.

APPENDIX II

WHO International Standards For Water, 1971 (75)

Substance	Maximum Permissible Level (g/m^3)	
	For Domestic Use	For Drinking Water
Arsenic (as As)*	-	0.05
Calcium (as Ca)+	200.0	
Cadmium (as Cd)*		0.01
Chromium (as Cr)*	0.05	
Copper (as Cu)	1.5	
Iron (total Fe)	1.0	
Lead (as Pb)*		0.1
Magnesium (as Mg)	150.0	
Manganese (as Mn)	0.5	
Mercury (total Hg)		0.0001
Selenium (as Se)*		0.01
Zinc (as Zn)	15.0	
Ammonia		0.5
Anionic detergent	1.0	
Chloride (as Cl)	600.0	
Cyanide (as Cn)*		0.05
Fluoride (at 10-12°C)+		1.7
Mineral oil	0.3	
Nitrate (as NO_3)+		45.0
Total nitrogen (exclusive of NO_3)		1.0
Phenol*	0.002	
Polynuclear aromatic hydrocarbon (PAH)		0.2
Sulphate (as SO_4)	400.0	
Radionuclides-gross α activity		3pCi/L
Radionuclides-gross β activity+		30pCi/L
Caliform bacteria		Not more than 10/100ml
BOD		6
COD	-	10.0
pH	6.5-9.2	
Total hardness (as $CaCO_3$)	500.0	
Total dissolved solids	1500	

*Highly toxic. +Harzardous to health (1pCi = 1×10^{-12} curie).

APPENDIX III

Full Results Of Determinations

APPENDIX III(a)

pH (pH Units)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	6.8	7.2	7.2	7.5	7.8	7.4	7.6	7.7	7.6	7.2	7.4
2	9.2	7.1	7.2	7.7	8.0	7.8	8.6	7.8	7.3	7.6	7.8
3	6.2	7.2	7.2	7.4	7.8	7.9	7.6	9.0	7.4	8.0	7.6
4	8.2	7.2	7.4	7.6	8.1	7.4	8.2	9.2	7.6	7.9	7.9
5.	7.2	7.3	7.6	7.4	9.1	7.9	7.8	9.2	7.5	7.8	7.9
6	7.6	7.2	7.8	7.5	8.2	7.9	9.1	8.9	7.8	7.6	8.0
7	7.6	7.1	8.0	7.6	9.0	7.9	8.6	9.0	7.6	7.7	8.0
8	8.0	7.6	8.2	7.8	8.6	8.2	7.9	8.7	7.5	7.9	8.0
9	9.4	8.8	10.0	8.8	9.6	9.2	9.6	9.5	9.1	8.9	9.3
10	7.3	6.9	7.8	7.7	8.3	7.6	7.8	7.9	7.8	7.5	7.7

APPENDIX III(b)

Conductivity (μscm^{-1})

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	45.0	47.8	55.0	62.5	64.0	65.0	67.0	62.5	63.0	65.5	59.7
2	80.1	81.8	98.5	86.5	100.0	97.5	106.0	90.5	97.5	10.2	94.0
3	89.0	85.0	83.9	86.5	90.0	94.5	94.5	102.5	85.0	91.0	90.2
4	85.0	87.0	86.5	88.5	94.0	98.5	99.0	102.7	87.0	93.5	92,2
5	95.0	86.5	86.7	87.5	102.0	98.0	93.5	102	83.5	89.0	93.4
6	95.0	85.9	92.8	87.0	94.0	94.0	110	101	86.5	87.0	93.3
7	100	83.2	86.0	87.0	102	99.0	97.0	100	85.0	85.0	92.4
8	75.0	9.1	100.4	91.0	102.5	96.0	94.0	97.5	86.9	89.0	93.1
9	100	102	105	99.5	108.2	102	114	104.4	92.5	94.0	102.2
10	65.0	64.8	65.3	71.5	72.5	70.5	73.0	67.5	70.5	71.0	69.2

APPENDIX III(c)

Total Residue (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	150	125	88	103	96	106	99	99	95	93	105.4
2	93	81	94	85	92	91	82	85	88	89	88.0
3	75	91	69	88	81	82	82	89	75	87	81.9
4	106	87	76	90	64	83	81	93	74	87	84.1
5	73	77	76	86	83	80	86	89	81	89	82.0
6	93	91	73	88	86	89	94	87	80	90	87.1
7	112	77	85	79	77	91	85	83	88	88	86.5
8	88	93	88	94	80	84	80	88	85	87	86.7
9	119	94	88	89	83	94	87	97	87	95	93.3
10	407	358	312	325	326	298	295	289	267	274	315.1

APPENDIX III(d)

Filtrable Residue (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	139	121	82	97	84	91	84	89	85	83	95.5
2	70	79	81	81	80	89	77	74	81	84	79.6
3	69	87	69	79	73	74	73	83	67	79	75.3
4	83	77	69	79	63	75	78	83	64	82	75.3
5	65	73	69	71	79	75	70	83	65	81	73.1
6	78	89	69	77	78	77	77	81	69	79	77.4
7	78	73	65	66	70	75	71	81	73	76	72.8
8	79	80	73	77	75	82	74	79	75	81	77.5
9	95	77	83	85	78	87	83	88	75	83	83.4
10	381	320	309	319	310	281	271	271	259	256	297.7

APPENDIX III(e)

Suspended Residue (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	11	4	6	6	12	15	15	10	10	10	9.9
2	23	2	13	4	12	2	5	11	7	5	8.4
3	9	4	6	9	7	8	9	6	8	8	7.4
4	23	10	7	11	1	8	3	10	10	5	8.8
5	8	4	7	15	4	5	16	5	16	8	8.8
6	15	2	4	11	8	12	17	6	11	11	9.7
7	34	4	20	13	7	16	14	2	15	12	13.7
8	9	13	15	17	5	2	6	9	10	6	9.2
9	24	17	5	4	5	7	4	9	12	12	9.9
10	26	30	3	6	16	17	24	18	8	18	16.6

APPENDIX III(f)

Chloride (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	9.4	5.5	5.0	5.0	8.5	6.5	8.5	5.0	6.3	5.0	6.5
2	12.7	7.2	10.0	10.0	11.5	18.5	14.5	12.5	10.0	10.0	11.7
3	10.0	11.5	10.0	10.0	11.5	15.0	10.0	10.0	10.0	5.5	10.4
4	6.5	10.0	10.0	10.0	10.0	16.5	10.0	10.0	10.0	6.0	9.9
5	8.5	12.7	10.0	8.5	10.0	15.0	10.0	10.0	10.0	5.5	10.0
6	17.7	11.1	10.0	10.0	10.0	16.5	11.5	10.0	10.0	9.8	11.7
7	10.0	8.5	6.5	11.5	10.0	18.5	10.0	10.0	10.0	7.5	10.3
8	11.5	10.0	8.5	11.5	10.0	15.0	10.0	9.5	10.5	8.0	10.5
9	11.1	11.1	8.5	8.5	10.0	20.0	10.0	10.0	12.5	10.5	11.2
10	7.2	5.5	6.0	6.5	5.0	5.0	5.0	5.0	5.0	4.0	5.4

APPENDIX III(g)

Fluoride (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	1.0	3.0	1.0	3.0	2.0	2.0	2.0	2.0	2.0	3.0	2.1
2	2.0	1.0	2.0	2.0	2.0	2.0	2.0	2.0	3.0	3.0	2.1
3	1.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	3.0	3.0	2.1
4	2.0	2.0	2.0	2.0	1.0	3.0	2.0	2.0	2.0	3.0	2.1
5	1.0	2.0	2.0	1.0	2.0	1.0	3.0	2.0	2.0	3.0	2.4
6	2.0	3.0	2.0	2.0	2.0	2.0	3.0	2.0	2.0	4.0	2.4
7	2.0	2.0	2.0	1.0	2.0	2.0	3.0	2.0	2.0	3.0	2.1
8	2.0	2.0	2.0	1.0	1.0	2.0	3.0	2.0	2.0	3.0	2.0
9	2.0	2.0	1.0	1.0	2.0	2.0	3.0	3.0	2.0	3.0	2.1
10	7.0	8.0	6.0	5.0	7.0	7.0	5.0	4.0	7.0	6.0	6.2

APPENDIX III(h)

Iodide (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	-	.012	.030	.450	.295	.052	.152	.105	-	.099	.120
2	.105	.012	.082	.65	.46	.183	.195	.105	.082	.185	.206
3	.076	.050	.099	.45	.31	.215	.31	.010	-	.185	.171
4	.105	.185	.030	.35	.278	.109	.31	.152	-	.190	.171
5	.105	.030	.270	.225	.225	.152	.225	.130	-	.155	.152
6	.130	.050	.055	.225	.365	.170	.227	.160	.052	-	.143
7	.050	.250	.185	.270	.215	.075	.372	.109	-	.105	.163
8	.395	.030	.082	.192	.242	.178	.110	.150	.175	.105	.166
9	.130	.060	.082	.270	.350	.152	.195	.185	-	.170	.159
10	.040	.060	.099	.215	.190	.052	.082	.082	.030	.082	.093

APPENDIX III(i)

Sodium (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	3.1	3.1	4.2	4.8	4.5	4.7	4.2	4.7	4.6	4.4	4.2
2	2.5	3.0	3.8	4.5	4.4	4.6	4.2	4.4	4.8	4.5	4.1
3	2.2	3.0	4.0	4.3	4.4	4.5	4.1	4.5	4.6	4.4	4.0
4	2.6	3.4	3.9	4.5	4.4	4.6	4.1	4.4	4.7	4.5	4.1
5	2.4	3.3	3.8	4.3	4.4	4.6	4.2	4.3	4.8	4.4	4.1
6	2.2	2.8	3.7	4.4	4.4	4.4	4.2	4.3	4.7	4.2	3.9
7	2.0	3.2	3.6	4.4	4.3	4.4	4.2	4.5	4.5	4.2	3.9
8	2.3	3.5	3.8	4.5	4.3	4.2	4.3	4.4	4.5	5.0	4.0
9	2.7	3.1	4.0	4.3	4.4	4.4	4.2	4.5	4.7	4.2	4.1
10	3.9	4.1	4.1	4.6	4.1	4.1	3.6	3.9	3.8	3.4	4.0

APPENDIX III(j)

Potassium (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	5.4	5.0	5.2	5.5	5.3	5.2	4.7	5.5	4.8	4.6	5.1
2	4.5	4.6	5.1	5.2	5.1	4.9	4.8	4.8	4.8	4.6	4.8
3	4.5	4.6	5.0	5.0	5.2	4.7	4.6	4.9	4.7	4.5	4.8
4	4.6	4.4	5.0	5.0	5.2	4.7	4.8	4.7	4.6	4.7	4.8
5	4.4	4.2	5.0	5.0	5.1	5.0	4.7	4.6	4.7	4.6	4.7
6	4.4	4.1	4.9	4.8	5.1	4.9	4.6	4.5	4.8	4.5	4.7
7	4.4	4.2	4.8	4.8	5.1	4.9	4.6	4.6	4.7	4.6	4.7
8	4.8	4.5	4.9	4.9	5.1	4.9	4.8	4.7	4.9	5.6	4.9
9	4.7	4.6	6.2	4.9	5.2	5.1	4.7	5.0	4.9	4.7	5.0
10	7.2	7.1	9.0	9.1	8.7	8.0	8.2	8.2	8.0	8.1	8.2

APPENDIX III(k)

Calcium (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	2.7	5.3	4.8	4.5	3.0	2.0	2.7	3.3	2.7	3.8	3.5
2	10.7	12.9	4.8	7.8	7.8	4.7	3.3	6.0	3.3	8.3	7.0
3	4.9	12.9	4.8	4.5	4.5	4.0	4.0	3.3	2.7	7.0	5.3
4	10.7	14.0	3.8	3.3	5.3	4.0	3.3	4.0	4.7	6.2	5.9
5	6.6	13.3	4.8	3.3	6.3	3.3	2.7	6.0	2.0	7.4	5.6
6	7.5	14.8	5.0	4.5	4.8	2.7	2.7	4.0	4.0	6.2	5.6
7	6.6	12.3	4.8	1.2	6.0	2.7	3.3	3.3	3.3	5.9	4.9
8	7.9	15.0	4.8	3.3	6.0	2.7	2.8	3.2	3.4	7.0	5.6
9	11.1	17.9	4.7	3.3	7.5	3.3	3.3	3.3	4.0	7.9	6.7
10	3.4	8.2	6.0	2.3	2.1	1.4	2.7	2.7	2.7	4.2	3.6

APPENDIX III(1)

Magnesium (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	0.90	1.17	1.27	1.14	3.15	2.4	5.0	4.00	3.50	3.25	2.58
2	1.03	1.13	1.20	1.23	3.10	2.62	5.0	4.00	3.50	2.75	2.56
3	0.95	1.17	1.30	1.38	3.1	2.4	5.0	4.50	3.50	2.50	2.58
4	0.97	1.03	1.23	1.24	3.0	2.2	5.0	3.00	3.5	2.5	2.37
5	0.95	1.10	1.17	1.29	3.1	2.38	4.5	4.0	3.0	2.50	2.40
6	0.90	1.20	1.20	1.23	3.0	2.15	4.0	3.5	4.5	2.75	2.40
7	1.10	1.13	1.27	1.28	2.9	2.38	4.0	4.0	4.0	3.0	2.51
8	0.90	1.07	1.27	1.24	2.85	2.20	4.50	4.2	3.5	2.25	2.40
9	0.83	0.93	0.77	1.20	2.85	2.00	2.50	3.0	2.0	2.25	1.83
10	1.0	1.25	1.37	1.52	3.8	2.40	4.0	4.5	4.5	3.0	2.73

APPENDIX III(m)

Iron (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	4.75	1.48	0.85	1.55	1.2	0.85	0.5	1.0	0.85	1.40	1.44
2	0.70	1.10	0.75	0.70	0.36	0.85	0.85	0.70	0.70	0.85	0.76
3	1.1	0.85	0.70	0.70	0.70	0.85	0.70	0.50	0.85	0.85	0.78
4	0.50	0.85	0.5	0.70	0.70	0.36	0.70	0.85	0.35	0.85	0.64
5	0.17	1.25	0.35	0.70	0.36	0.55	1.4	0.70	0.35	0.85	0.67
6	0.75	1.70	0.35	0.85	0.36	0.85	0.70	0.70	0.50	1.25	0.80
7	0.74	0.90	0.35	0.36	0.55	0.20	0.85	0.50	0.35	0.85	0.57
8	1.26	1.75	0.18	0.70	0.55	0.55	0.70	0.75	0.40	0.85	0.77
9	0.70	2.22	0.26	0.55	0.55	0.70	0.85	0.50	0.35	1.0	0.77
10	2.87	2.38	0.42	0.55	0.36	0.36	1.05	0.70	0.20	0.85	0.97

APPENDIX III(n)

Zinc (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	2.19	0.66	0.05	0.1	0.09	0.09	0.1	0.09	0.1	0.1	0.36
2	0.07	0.12	0.35	0.17	0.09	0.40	0.12	0.09	0.07	0.08	0.16
3	1.92	0.42	0.04	0.03	0.07	0.1	0.12	0.07	0.06	0.07	0.29
4	1.77	0.62	0.32	0.09	0.06	0.12	0.09	0.04	0.12	0.07	0.33
5	1.65	0.38	0.07	0.03	0.07	0.04	0.04	0.04	0.07	0.09	0.25
6	0.68	2.06	0.55	0.82	0.71	0.86	0.84	0.80	0.90	0.71	0.89
7	2.02	0.58	0.06	0.04	0.07	0.13	0.09	0.12	0.07	0.07	0.33
8	1.02	0.43	0.07	0.09	0.09	0.09	0.06	0.07	0.08	0.09	0.21
9	2.16	0.38	0.34	0.17	0.15	0.68	0.57	0.53	0.60	0.64	0.62
10	1.79	0.66	0.06	0.03	0.09	0.09	0.09	0.12	0.10	0.07	0.31

APPENDIX III(o)

Lead (ppm)

S/N	Collections										P/A
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	
1	0.21	0.1	0	0	0.5	0	0.24	0.24	0	0.1	0.14
2	0	0.1	0	0	0.1	0	0	0	0	0	0.02
3	0	0.2	0	0	0.1	0	0	0	0	0	0.03
4	0	0	0	0	0	0	0	0	0	0	0.0
5	0	0	0	0	0	0	0	0	0	0	0.0
6	0	0	0	0	0	0.1	0	0	0.1	0.1	0.03
7	0	0	0	0	0	0	0	0	0.2	0	0.02
8	0	0	0	0	0	0	0	0	0	0	0.0
9	0	0	0	0	0	0	0	0.1	0.09	0	0.02
10	0.5	0.5	0	0.1	0.35	0	0.24	0.5	0.36	0.2	0.28