FLUORIDES IN LOCAL WATER SUPPLIES

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BY

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THIS PROJECT THESIS IS DEDICATED TO MY BELOVED PARENTS.

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INTRODUCTION

A great deal of attention has been given to the concentration of naturally occuring fluorine in water, especially drinking water, following the publication of certain medical and dental researches on its effect on the formation and decay of teeth. It has been established that excess fluorine produces mottling of the teeth and in extreme cases fluorosis of the bone structure. Very low concentration or lack of fluorine results in bad teeth formation and dental decay particularly in children with ages less than eight years.

THE THEORY OF FLUORIDATION

A. INTRODUCTION

Fluoridation is the practice of adding suitable fluorides to public water supplies as a means of reducing the incidence of dental caries.

Waters containing less than 0.7 ppm fluorine concentration have to be reinforced with further addition of fluorine to raise it to a suitable balance in the water supply system. It is generally accepted that the addition of inorganic fluorine compounds to water will give it the same properties as naturally occuring fluorides. The presence of fluoride in average concentrations greater than two times the optimum values shown in table 1 shall constitute grounds for rejection, but where fluoridation is practiced the average fluoride concentration shall be kept within the upper and lower limits shown in the table. The threshold of toxicity appears to be 1.0 to 1.5 ppm and the incidence and severity of fluorisis vary with the concentrations.

TABLE 1: Showing Recommended Control Limits of Fluorine with Respect to the Daily Temperature of Air.

Annual Average of Maximum Daily Air Temperature ^{o}F	Recommended Control Limites of Fluorine Concentration in mg/L.		
	Lower	Optimum	Upper
50.0 to 53.7	0.9	1.2	1.7
53.8 to 58.3	0.8	1.1	1.5
58.4 to 63.8	0.8	1.0	1.3
63.9 to 70.6	0.7	0.9	1.2
70.7 to 75.2	0.7	0.8	1.0
75.3 to 90.5	0.6	0.7	0.8

The temperature data was obtained for a maximum period of five years.

B. THE PRACTICE OF ADDING FLUORIDES TO WATER SUPPLIES

Controlled adjustment of the fluoride concentration of drinking water supply was started in the U.S. in 1945. Three Communities, Michigan, New York and Ontario were selected for the process and in each, a naturally occuring fluoride level of 0.1 ppm was supplimented by a fluoride level of 1 ppm. The findings were compared with data from adjacent control communities where nature has provided an optimum fluoride level. Remarkable uniformity and consistency resulted from these comparisons on which the following conclusions were reached:

(i) Controlled fluoridation has the same inhibitory effect on dental caries as naturally occuring fluorides in the drinking water.

(ii) The maximum benefit of caries inhibition is obtained by those who used drinking water fluoridated from birth, and the benefits persist through adulthood.

(iii) Teeth that have erupted before the commencement of fluoridation showed little reduction in their vulnerability to dental caries.

(iv) Fluoridating a community water supply has an annual cost range of 4 to 14 cents per person with an average of 10 cents.

(v) A relatively simple technical procedure involving chemical feeding equipment and testing apparatus, being in standard use in water plants, is all that is needed to maintain an optimum and constant fluoride ion concentration in drinking water.

(vi) All fluoridation studies have added support to the conclusion that optimally fluoridated drinking water in a range of 0.7 to 1.3 ppm is a safe, relatively simple and practical public health measure that effects a $\frac{2}{3}$ reduction in the incidence of tooth decay with a significant reduction in the loss of teeth from dental caries.

The approval and endosement of controlled fluoridation by national, state and local public health agencies, professional health associations and a wide range of organisations that have

considered health as an important aspect, was based upon the relationship of fluorine to dental health and health in general . In the U.S. more than 3000 communities with a population of about 60 million have adopted controlled fluoridation, these include Baltimore, Buffalo, Cleveland, Chicago, Detroit, Milwaukee, New York, Philadelpia, Pittsburgh, San Francisco, St. Louis and Washington D.C.

C. OTHER FORMS OF FLUORIDE APPLICATION

i. The solid form administration of fluoride - fluoride tablet.

Where no fluoridation is practiced and the water supply has a naturally low fluoride level a daily supplement of 0.5 mg fluoride during the first 2 to 3 years of life and 1.0mg thereafter is an acceptable alternative. The natural fluoride level of the drinking water must be determined and the tablets must be taken under prescription. Fluoride supplimentation by this method has not been subject to extensive clinical testing but analysis of data from several studies indicates that the dental benefits are similar to those obtained with optimally fluoridated drinking water.

ii. The topical application of fluoride.

The application of fluoride solutions to the cleansed, dried enamel surfaces of the teeth results in a 40 to 50% reduction in the incidence of dental caries among children. The applications should be made soon after teeth have erupted and should be repeated in accordance with the tooth eruption pattern of the child. The solutions most frequently used

are 2% sodium fluoride and 8 to 16% stannous fluoride, but such applications are not preferred to fluoridation of drinking water even though they are effective and useful. The applications require individual, personal and time consuming services, they must be repeated at regular intervals and are much more expensive than water fluoridation. The use of topical fluoride is considered as an alternative to fluoridation or for children whose teeth have erupted before the commencement of fluoridation.

iii. The incorporation of fluoride in dentifrices.

The progressive usage of therapeutic dentifrices has induced a significant portion of the population to adopt routine usage of fluoride containing dentifrices, most of which are provided with a fluoride concentration of 1.0 mg per 1.0 gm. An average of 20% of the fluoride in a single brushing containing 2.0 mg per 1.0 gm of dentifrice was retained by subjects of from 4 years to adulthood but not more than 0.4 gm fluoride would be retained from each brushing. The usage and availability of these products have aroused some interest regarding the systemic metabolism of their fluoride content. In a study carried out on rats only 30% of the fluoride ingested was absorbed from the gastrointestinal tract and about 81% was retained in the carcasses.

D. COMPOUNDS USED AS SOURCES OF FLUORINE

i. Occurence of fluorine.

It has been estimated that fluorine is the 19th

element in order of relative abundance and its content in the igneous rock which constitute 90% of the first 10 miles of the earth crust is about 600 ppm. The major natural fluorine containing minerals are cryolite, fluorspar and fluorapatite, their estimated fluorine content percentages are 54.5, 48.5 and 3.8 respectively.

The most important of the three is fluorspar because of its occurence in many countries and its capability of being produced in various grades to satisfy certain requirements. The grades are metallugical grade, ceramic grade and acid grade.

ii. Fluorine Compounds used for Fluoridation.

The most commonly used compounds for fluoridation are sodium silicofluoride and sodium fluoride but other chemicals such as magnesium silicofluoride, ammonium silicofluocate, calcium fluoride, hydrofluosilicic acid and hydrofluoric acid can also be used. These can be added to water in a solution or solid form but solution additions are more suitable for small water works while dry feeding is more acceptable to larger installations where gravimetric dry feeders can be used.

There is a slight loss of fluorine amounting to about 0.2 ppm if the chemical is added before filtration, there is also an appreciable loss of fluorine when high magnesium waters are lime softened, therefore it is more advantagious to add fluorine to the filtered water in the treatment

plants. The optimum residual fluorine in the treated water should be between 1.0 to 1.3 ppm and it is necessary to control the dose accurately and conduct tests on the residual fluorine in water that is being distributed. Extreme care must be exercised in the handling of fluorine compounds since they are potentially dangerous in large doses.

E. PLANTS USED FOR FLUORIDATION

The equipment for dealing with fluorides should be such that it does not allow the compound to come into contact with the operators skin or to be inhaled by him. Protective masks and clothing must be used and the plants may be designed such that the operator passes through a cloak and washing room before and after work.

In each of the methods used for the addition of the fluorine compound to the water the addition takes place after the water has undergone the purification stage.

i. The method of adding fluorine compounds to water in a solution form is by means of solution or part suspension feeders consisting of tanks and measuring devices fitted with chart recorders. Dust formation must be avoided by the use of special equipment to handle the fluoride bags. Suitable precaution must also be taken to prevent the deposition of hardness salts due to the softening action of the fluoride salts.

ii. This method involves the use of gravimetric dry feeders fitted with chart recording devices which keep a record of how much fluorine has been added to the water. The method is more suited to temperate climates but when installed in humid tropical climates the equipment must be placed in completely air conditioned rooms and the fluoride store must be similarly treated. The vehicle for the fluoride which is normally water must be softened to prevent the deposition of hardness forming salts in the tanks and the pipe lines.

Small plants for residential fluoridation are being marketed and some of them use sodium fluoride, potassium or fluorspar. The plants are installed under rental agreement in which the distributor instals, checks and services the plant periodically. Any installation employing the toxic fluoride should be undertaken by a competent person and its operation should be periodically observed. Those employing fluorspar have an inherent safety factor in the very low solubility of the chemical and hence are condusive to safe handling.

F. PUBLIC REACTION AGAINST FLUORIDATION

The practice of fluoridation originated in the U. S. around 1945, but in Great Britain it wasn't until 1952 when interest in the idea became strong enough to warrant the sponsorship of a government mission to the U.S. to study fluoridation. As a result of this mission a report "The fluoridation of public water supplies in North America as a

'olling dental caries" was published in 1953,
that fluoridation should be considered after
ctive trials, hence four water authorities
s suitable for the trial work.
y the public became aware that such a project
d upon there arose an intense protest which
was never experience in the water works. As a result of this opposition certain proposals streneously survived while others had to be completely abandoned, the following examples indicate the strength of opposition.

The first authority to start fluoridation was the County water authority of Anglesey in November 1955 and only the zone supplied from the Gwalchmai reservoir was treated, the Bodafon untreated zone served as a control. No undue opposition was encountered from the scheme even when in full operation.

Fluoridation at Watford commenced in May 1956 and the Sutton district water supply was used as a control. There was some amount of opposition but after the operation was began it became diminished.

The County Borough of Darlington agreed to participate in 1954, and by the next year the tender of the necessary plant was recommended but due to the pressure of public opinion the council had to abandon the project.

Fluoridation at Andover commenced in July 1956, but there was an immediate reaction from the public criticising

that the measure results in mass medication which is unethical. In July 1958 fluoridation ceased by the usual procedure of bringing the case before the council, prior to which an injunction was sought for by a number of tax payers to restrain the council from the practice.

The national farmers union sued Marston Valley Brick Company on behalf of one of its members whose 208 acre farm adjoins the brick company claiming that fluorine emitted with the chimney gases contaminated the grazing land and as a result the cattle didn't grow properly, their milk production was reduced, their teeth rot and their skeleton was adversily affected.

In the U.S., a small but actively vocal group of opponents of water fluoridation claimed that fluorides are poisonous hence the measure was dangerous and harmful and that it results in mass medication which is a compulsory health measure, therefore it is illegal and unconstitutional. This opposition was not based on any scientific evidence or support from any court of law but it defeated many fluoridation proposals conducted all over the country.

G. DEFLUORIDATION

For all practical purposes 1.5 ppm fluoride in water is considered to be the safe upper limit. If water which contains excessive fluoride is ingested over a long period a condition known as dental fluorisis arises, it causes brown mottling of the teeth. The defect cannot be corrected and there is a tendancy that the enamel may be lost through attrition.

Many methods were suggested as alternatives for the removal of excess fluoride from water, some of these are:

i. Magnesia in conjunction with lime softening.

A hard water containing substantial quantities of magnesium and less than 4 ppm fluoride can be treated with lime for fluoride removal. It may be necessary to add more magnesium to combine with the fluoride before precipitating the magnesium with the lime. 45 to 65 ppm of magnesium is necessary to reduce the fluoride by 1ppm, high temperature may also be necessary.

The excess lime treatment of magnessium waters has a side effect of reducing the quantity of fluoride. Scott and Associates have suggested a relationship associating removal to adsorption of fluoride on magnesium ion, hence the following formula was developed.

$$P = 7\sqrt{Mg}$$

where P = percentage removal of fluoride

Mg = milligrams per litre of precipitated magnesium.

For example, a reduction of 3.3 mg/l fluorine to 1 mg/l requires the precipitation of 100 mg/l of magnesium ion, if there is insufficient quantity of magnesium its salt may be added to achieve the desired flucride removal.

ii. Tricalcium phosphate.

Bone has been specially prepared for fluoride removal, it can be regenerated by treatment with caustic soda followed by an acid wash, similarly bone charcoal can also be used. Tricalcium phosphate prepared from milk of lime and phosphoric acid has been used in contact filters and regeneration was by 1% caustic soda followed by dilute hydrochloric acid or carbon dioxide treatment to neutralise excess alkaline. The removal capacity is about 300 grains of fluoride per cubic foot of bed.

iii. Ion exchangers.

There is a number of ion exchange materials that can be used, one of which is organic resinous ion exchange medium selected for fluoride, it removes only those metals which produce insoluble hydroxides. The exchange capacity is about 1240 grains per cubic foot of bed with high chemical costs of regeneration.

Processed tricalcium phosphate composed of granules of

$Ca_3 P_2 O_8 - 8 H_2O$ and $Ca_3 P_2 O_8 . Ca (OH)_2$

is found to remove fluoride by ion exchange, regeneration and removal requirements are as stated below:

a. Anion exchanger

Tricalcium phosphate.

b. Exchange capacity

Observed Kilograins per cubic foot as calcium carbonate

0.4 to 0.9 fluoride.

Observed gramequivalent per cubic foot

1.3 to 3.0

Regenerator

Na OH and H cl.

c. Regeneration requirements

Observed lb/Kg exchanged	0.7 to 1.7
Observed equivalent/equivalent exchanged	2.6 to 6.2
Theoretical lb/Kg exchanged	0.275

iv . Activated carbon particles.

Activated carbon is quite efficient on removing fluoride but a pH of less than 3.0 is necessary, no removal takes place at pH 8 and above, regeneration is by weak acids and alkaline solutions.

v . Adsorption with aluminium compounds.

Alum floc has been used for removing fluoride, 300 to 500 ppm of the coagulant is necessary to remove 4 ppm of fluoride, control for optimum pH is necessary.

1. THE SUPPLY OF FLUORINE THROUGH WATER

A. INTRODUCTION

Elemental fluorine is rarely if ever found in nature due to its violent chemical reactivity and apart from the comparatively small amounts of manufactured gaseous fluorine the element is found in the industry, as in nature, as fluorides. Organic fluorochemicals are increasing in volume and importance though the inorganic materials consitute a larger proportion of the manufactured fluorides.

The relative position of fluoride in the order of abundance of elements of the earth crust justifies its presence in sea water, numerous supplies of drinking water, deposits of fluorspar, cryolite and fluorapatite, and in surface dust found close to the mineral deposits. The principal sources of supply of fluorine available to the physiology of man are water, some species of vegetation, certain edible marine animals, dusts and certain industrial processes.

The fluoride present in many supplies of drinking water largely lends the effects of fluorides on human health.

B. INGESTION OF FLUORINE FROM WATER

Water is an essential nutrient required by man and other forms of life for a variety of functions including regulation of body temperature, being a solvent and a vehicle for other nutrients and waste products through the vascular system and the intra cellular spaces. The requirement vary

on individuals under the influence of internal or external stimuli, it is continous and must be maintained appropriately.

The water that is available for the utility of man is regarded as impure because it contains a variety of other substances, including fluoride, in suspension or in solution to a greater or lesser degree.

i. Origins of fluoride in water.

The normal source of water for man is sea water which contains significant quantities of fluoride variously recorded as 0.8 to 1.4 ppm. Appreciable quantities of halogens escape from the sea into the atmosphere through droplets of sea water being caught up by wind as spray or being oxidised by ozone and liberated in the gas form which eventually incoperate into the rain or precipitation and is carried to the land.

A wide distribution of fluorides takes place in the atmosphere originating from dusts of fluoride containing soils, gaseous industrial wastes, the burning of coal fire in populated areas and the gases given off in areas of volcanic activity which may contain considerable quantities of fluoride so that the fluoride levels of rain in such areas may also be substantially increased.

The amounts of fluoride derived from the solvent action of water on rocks and soils is considerably higher than those from the atmosphere. The fluoride content of surface and

underground water depend on factors such as availability and solubility of parent mineral, porosity of rocks or soils through which the water passes, temperature of interaction between rock and water and pH of the water. In alkaline and hotter waters found in volcanic areas the fluoride level tends to be higher.

ii. Chemistry of fluoride in water.

When a fluoride compound is dissolved in water the element fluorine would be present as fluoride ion depending on the ionic concentration and pH of the water, the fluoride would also be present in solution as hydrogen fluoride (HF_2^-) and undissociated hydrogen fluoride (HF). In dilute solutions at neutral pH virtually all the fluoride would be present as fluoride ion but as the pH decreases the proportion of fluoride ion decreases while the proportion of HF_2^- and undissociated HF increases. This does not mean that different fluoride compounds would yield fluoride that differs according to its source, assuming that calcium fluoride is representitive of natural fluorides and sodium fluoride is representitive of artificial fluorides, it would be found they ionize as shown in the equation below when dissolved in water:

(a) Calcium fluoride

$$CaF_2 \longleftrightarrow Ca^{++} + 2F^-$$

$$F^- + H^+ \longleftrightarrow HF$$

$$HF + F^- \longleftrightarrow HF_2^-$$

(b) Sodium fluoride

$$NaF \longleftrightarrow Na^{+} + F^{-}$$

$$F^{-} + H^{+} \longleftrightarrow HF$$

$$HF + F^{-} \longleftrightarrow HF_2^{-}$$

In both cases fluoride exists in the forms of F^{-}, HF and HF_2^{-} which would be chemically and physiologically identical irrespective of which of the two compounds they are derived from.

C. INTAKE OF FLUORIDE FROM DRINKING WATER

The degree of fluoride concentration and the quantity of water consumed directly controls the amount of fluoride intake from water. An assessment of fluoride intake from water containing 1.0ppm gives a range between 0.39 to 1.17mg fluoride daily in children between the ages of 1 to 12 years depending on the individual water requirement. Another assessment gave 1.0ml of water per 1 calorie of energy as a measure of the daily water requirement in the diet consumed by children in the stated age group, this was further analysed to range between 390 to 1166ml of water daily.

Climatic conditions such as mean annual temperature, excessive day time temperatures, radiant heat gain, relative humidity and wind movement affect the water intake.

Age - years	1 to 3	4 to 6	7 to 9	10 to 12
Bodyweight -Kg	8 to 16	13 to 24	16 to 35	25 to 54
From drinking water-mg	0.39-0.56	0.52-0.75	0.65-0.93	0.81-1.17
From food-mg	0.03-0.27	0.04-0.36	0.05-0.45	0.06-0.56
Total-mg	0.42-0.83	0.56-1.11	0.70-1.38	0.87-1.73
Total-mg/Kg of body weight	0.03-0.10	0.02-0.09	0.02-0.07	0.02-0.07

TABLE 2: Estimated daily intake from food and drinking water.

D. INHALATION FROM VAPOURS

Considerable amounts of fluoride are ingested through various media in the inorganic form as elemental fluorine in gaseous Compounds or vapours and particulates dispersed in water. The organic fluorocompounds do not interfere with physiological effects of the inorganic fluorides.

i. The elemental fluorine.

Experimental animals were used to observe the effects of inhaling fluorine and results show that inhaling at a rate of 300ppm for a period of 3 hours or longer was fatal, at a rate of 100ppm with longer peroids an overall mortality of 60% was observed but with severe damage to the respiratory tract. Prolonged inhalation of fluorine produce chronic changes which are more severe than those induced by fluorides ingested in other methods. The direct contact of fluorine with the skin of animals and humans results in a violent reaction which produces a thermal type of burn.

At a level of 0.5ppm little or no pulmonary damage and dental tissue alteration was produced but a small increase in the fluoride

content of bones was observed. Animals exposed to the lowest test levels of hydrogen fluoride, 8.6ppm, showed no soft tissue damage but a considerable increase in the fluoride content of bones was observed.

Concentration of fluorine	Duration Days	Hours	Effect on animals
5ppm or more	18 to 19	95 to 160	Large numbers died-180 of 357
2ppm or less	31	176 to 178	Very few died - 10 of 148

TABLE 3: Results of inhaling gaseous fluorine by experimental animals.

. Particulate fluorides dispersed in water.

The inhaled particulate fluoride may be less important but it may add a very important amount of fluoride as a contaminant in the food or dispersed undissolved in water. According to some reports it plays a greater role in skeletal fluorisis than fluorides dissolved in water. Its acute effects have not been fully observed but a fatal case was reported in which inhalation of an aqueous mist evolved from sodium fluoride dissolved in high concentration in water was responsible. Effects of any kind induced by airborne fluorides are either from the atmospheric presence in the area of work or where they contaminate food, water or both.

E. ABSORPTION OF FLUORIDES

The present knowledge about fluoride absorption is based on numerous metabolic studies of experiments and observations in man. Information on children is limited but sufficient on the main factors governing absorption between young and adult humans, and it can safely be assumed that there are no differences in respect of mechanism site of fluoride.

Absorption of fluoride is governed by certain factors such as the nature of fluoride existance being organic or inorganic and the property of inorganic fluoride compound being soluble, insoluble or inert. Fluoride ions are released and absorbed depending on their solubilities hence forming basic effective tools of fluoride. The absorption of fluoride ions from an ingested dose of fluoride salt is rapid and the absorption from less soluble compounds is complete depending on solubility, physical properties of crystals, particle size and mode of intake. The inert fluoride compound is so stable that no fluoride ions are released or absorbed, it is completely excreted in the faeces and urine.

i. Fluoride ingested in drinking water.

Regardless of the level of fluoride in the water supply the absorption of soluble fluorides reaches 86 to 97%. Of the inorganic elements in drinking water calcium and magnesium pose as hardness of water to cause interference in fluoride absorption when present in sufficient quantities to bind with fluoride, these quantities range from 1.0 ppm in very soft waters to 100.0 ppm in very hard waters. In drinking water containing 1.0 ppm, 0.03 to 2.8% of the fluoride bound to calcium and 0.3 to 28% bound to magnesium relative to the hardness of the water. In drinking water containing up to 16.0 ppm with pH of 5 or higher the fluoride ions are available for almost complete absorption, 10 to 11% of the fluoride remains unabsorbed after 8 to 10 hours from administration.

The fluoride ions in beverages are derived from waters used for their preparation, and mineral waters and wines with fluorine content of 10.0 and 6.0 ppm respectively have a fluoride absorption as complete as that from plain water.

Table 4: Fluoride absorption in the adult human

Fluoride added	Period-weeks	Daily intake mg	Absorbed - %
Na F in water	14	6.47	97
" " "	2	12.40	97
" " "	2	19.40	96
CaF_2 in water	4	6.25	96
Cryolite in water	5	25.40	93

Fluorine containing organic compounds are not present in human diet or drinking water. The general forms of these compounds include fluoroacetates and fluorophosphates which are readily absorbed and highly toxic even in minute quantities, and fluorocarbons which are characterised by very low toxic effects.

TABLE 5: Fluoride Balance in Humans following Ingestion from Fluid and food.

Level in water supply - ppm	2	5.5	6.1	8.0	20
Age - years	35	55	57	57	30
Length of residence - years	10	29	34	19	8
Time of observation - years	96	60	133	140	45
Daily ingestion in fluid - mg	2.4	3.8	6.7	11.3	20.8
" " " food - mg	1.2	1.3	1.0	2.5	1.5
Total - mg	3.6	5.1	7.7	13.8	22.3
Daily excretion in faeces - mg	0.4	0.6	0.4	1.4	1.4
" " " urine - mg	2.9	4.5	8.1	10.4	12.3
Total - mg	3.3	5.1	8.5	11.8	13.7
Balance	+0.3	0	-0.8	+2.0	+8.0

F. COMMENT

The most effective way to ensure adequate fluoride consumption is by fluoridation of water as a measure to those drawing for drinking and cooking purposes from a central water supply system. With adequate nutrition enrichment of water to contain 1.0 to 1.2 ppm is desirable in temperate zones but in warmer regions the content should be smaller. Fluoridated drinking water is superior to other vehicles because it ensures a permanent and optimal ingestion.

For areas without a piped water supply system enriched cooking salt or flour may be suitable alternatives but precaution must be taken against introduction into fluoride

rich areas. The use of fluoridated milk, fluoride tablets and similar preparations is less promising due to consistency problems, but the administration of fluoride tablets with vitamins A and D to children may be feasible with many parents.

The outstanding ability of fluoride to prevent dental caries by mechanisms that are not yet fully understood warrant great efforts in research and practical application of methods that can be safely and effectively utilised to attain improved dental health.

2. FLUORIDE AND HUMAN HEALTH

A. INTRODUCTION

The chemical activity of fluoride ion makes it physiologically more active than any other elemental ion, it is the most electro nagetive of all elements. With low concentrations of fluoride ion enzymic processes may be either inhibited or stimulated and interaction between organic or inorganic body components that are of great importance to human physiology may occur.

Research into the biology of fluorides has shown that fluorides in very small doses have a remarkable influence on dental caries inhibition and higher doses result in the disturbance of enamel formation. The discovery of relation between high fluoride content of water and endemic mottling of the enamel of the teeth led to a research into fluoride and hard tissue physiology and pathology. Fluoride in very low doses effect over 50% reduction in the number of dental caries lesions and effects on the dental organ include influences on tooth form, appearance, eruption time, alignment in the dental arches and the frequency and severity of periodental diseases, all of which are found to be advantageous except for the mineralization disorder caused by excess fluoride.

Owing to its great affinity for calcium phosphate fluorine is the most exclusive bone seeking element, it is therefore accumulated in every tissue showing calcification though it is not found to aggravate pathological calcification. Fluorine is expected to play a positive role as a skeletal

stabilizer and its influences as such may provide a partial protection against senile osteoporosis which lead to serious fractures and invalidism. It is also expected that the optimal fluoride level for skeletal function and stability may be higher than that for the formation of dental enamel. There are indications that traces of fluorine are necessary for normal mineralization as are necessary for the formation of dental caries resistant enamel. Some reports suggested that since fluoride doses only twice those which affectively prevent dental caries may cause light disturbances of the calcification of the enamel and doses about twenty times greater cause damage to the skeletal system, it is imparative that great care must be exercised in the utilization of this powerful element.

Side effects from controlled fluoride ingestion in water can be regarded as unrealistic in nature because, for instance, allergy to fluoride has never been described among consumers of tea which is a fluoride-rich beverage.

Experience from human and animal chronic cases of fluoride poisoning and animal experimentation which supplemented for observations in man have contributed to the knowledge of the role of fluorine in human physiology and pathology.

Terminologically, fluoride denotes the ionized physiologically available form of the element and fluorine denotes the gaseous form but it may also be used to collectively denote the element in all its forms.

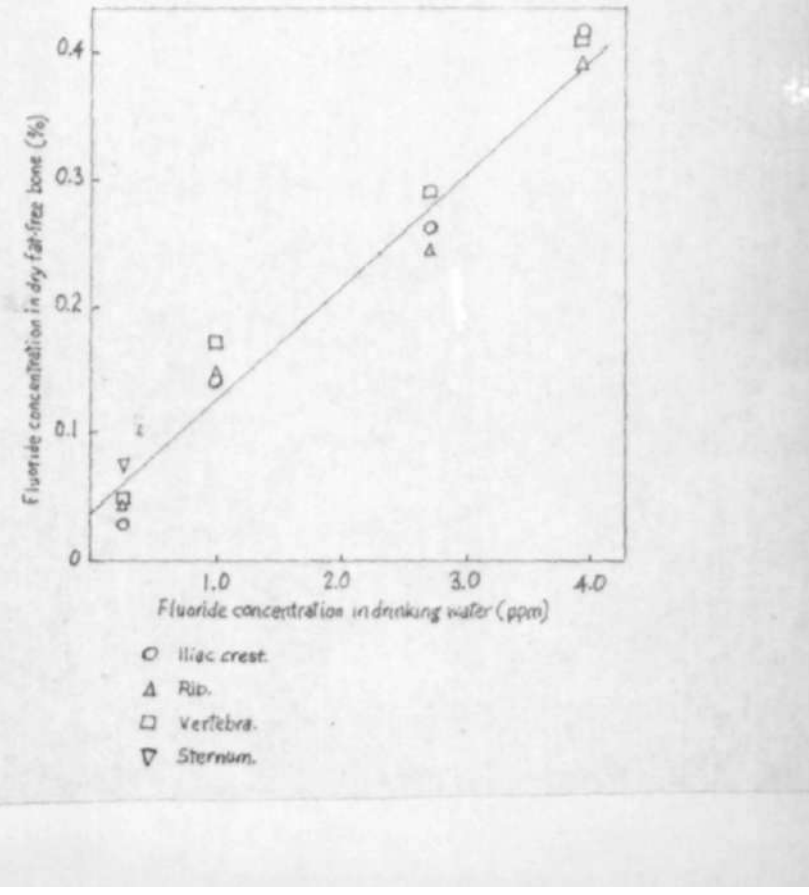
B. EFFECT OF FLUORIDE ON BONE AND HARD TISSUE

.Fluoride is a unique ion in that it continues to deposit in the calcified structures after the other constituents of the bone have already reached a steady state. A study following the ingestion of drinking waters containing less than 1.0, 1.0, 2.5 and 4.0 ppm indicated a ten fold increase of fluoride in bone, these findings being related to long term exposure of human to the fluoride levels. About 96% of the fluoride found in the body is deposited in the bones, this fact was responsible for the study of the effects of fluoride on the physical as well as the chemical structure of the bone. At levels of intake between 1.0 and 20.0 ppm upto 50% appears to be retained by the skeleton, most of the remainder is rapidly excreted via urine and faeces. Hardly any amount remains in the blood and soft tissues but a little may be found in pockets of calcification and the retained fluoride seems to be exclusively combined with mineralised tissues.

Chemical analysis of fluoride-rich tissues have shown that the incorporation of fluoride slightly alters the chemical composition of bone and tooth mineral, the carbonate and citrate contents are lowered, the calcium-phosphorus ratio remains unchanged and the magnesium level increases.

Fluoride was observed to enhance the crystal texture of the mineral phase of bone and the action is mainly attributed to the decrease in the citrate content of the bone with increasing fluoride concentration. It was also observed to

FIG. 1
RELATION OF FLUORIDE CONCENTRATION IN HUMAN BONES TO FLUORIDE LEVEL IN DRINKING WATER



enhance the seeding of apatite by precipitating at a lower concentration than would be expected. No direct evidence of the state of fluoride in calcified structures and the state of bond between organic and inorganic phases of bone has yet been shown.

i. Fluoride concentration of enamel in relation to caries.

It was reported that enamel from carious teeth contain a higher concentration of fluoride than surviving enamel from carious teeth but the concentration of dentine remains unchanged. Being influenced by the age of the subject, the difference in enamel fluoride accounts for the difference in caries resistance in areas with low fluoride concentration.

TABLE 6: Mean values for Carbonate and Fluoride Concentrations in Outermost Layers of Carious and non Carious Teeth.

Class of teeth	CO_2 - %		F - ppm		CO_2:F ratio	
	Carious	N.C.	Carious	N.C.	Carious	N.C.
From fluoride town						
Deciduous	2.09	1.90	202	369	1.05	0.51
Permanent	1.86	1.79	285	425	0.65	0.42
From non fluoride town						
Decidous	2.02	2.03	84	139	2.40	1.46
Permanent	1.84	1.83	176	183	1.04	1.00

N.C. = Non Carious, CO_2:F ratio = $\frac{\%\ \text{of}\ CO_2}{\text{F ppm}} \times 100$

ii. Mode of fluoride action in dental caries.

Fluoride plays a vital role in reducing the solubility of the enamel and inhibiting the bacterial enzymes responsible for producing the acid which is believed to attack the enamel. Some theories suggested that fluoride affects the protein matrix of the enamel and that it works in several ways such that certain mechanisms exist which have not so far been discovered.

iii. Relative importance of systemic and local effects of fluoride in caries.

Epidomiological studies on caries rates in subjects first receiving fluoride either before or after the eruption of their teeth have shown that the major effect is initiated from the intake of fluoride during tooth formation and the minor effect usually occurs when fluoride is received after the eruption of teeth. For instance,after ten years of fluoridation in Michigan the 16 year old group showed a 26% lower decayed - missing - filled rate than the controls as compared with about 60% reduction in rate of permanent teeth for children born after fluoridation. The fluoridation studies conducted by the Ministry of Health in Britain reported reductions of 26 and 14% caries in decidous teeth of 6 and 7 year old children five years after the commencement of fluoridation. The 3, 4 and 5 year old children whose teeth erupted under the influence of fluoride had reductions of 66, 57 and 50% respectively. The effect on caries rates in the teeth of mature adults that first received fluoride many years

after eruption is not known so far due to lack of information on such subjects.

The action on the solubility of enamel is partly due to fluoride deposited during formation, this may probably be supplemented by uptake on the enamel surface after eruption in which case anti enzymic effects exerted by fluoride are mostly local.

iv. Effect of fluoride on size and morphology of teeth.

Observations on human subjects and experimental animals have shown that fluoride has an influence on size and morphology of teeth, the effect might result in smaller teeth and shallower fissures affecting contact points and other food trapping areas. Several mechanisms by which fluoride could modify the morphology of teeth have been identified but the responsible mechanism is not known so far. It is believed that cusps formation depends on differential rate of enamel production influenced in the earlier stages of enamel development by local chemical

C. FLUORIDE AND DENTAL HEALTH

The relationship of fluorine to dental health has been a major subject of investigation for many years. Most, if not all, of the investigations have associated mottled enamel with fluoride level in drinking water and some have even established the quantitative nature of the relations between the fluoride level, mottled enamel and the prevalence of dental caries. In one of these investigations conducted in the U.S. involving about 7 million people ingesting water with a natural fluoride concentration of 0.7 ppm or more, certain conclusions were drawn with regard to the relationships.

(a) Excessive fluoride in the drinking water during the formation stages of enamel cause mottling and too low fluoride submits to prevalence of tooth decay.

(b) As the fluoride ion concentration increases from trace to about 1.0 ppm the prevalence of tooth decay decreases but further increases do not appreciably increase the dental decay preventive effect.

(c) An optimum fluoride level of about 1.0 ppm in temperate and 0.6 ppm in hot climates do not cause objectionable dental mottling.

(d) As the fluoride ion concentration increases above 1.5 ppm there is a progressive increase in the prevalence and severity of mottled enamel or dental fluorosis.

FIG. 2
RELATION BETWEEN DENTAL CARIES
& FLUORIDE CONTENT OF WATER

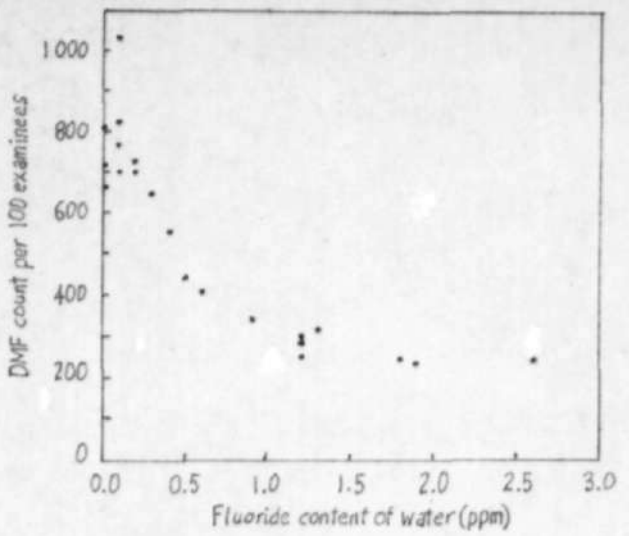
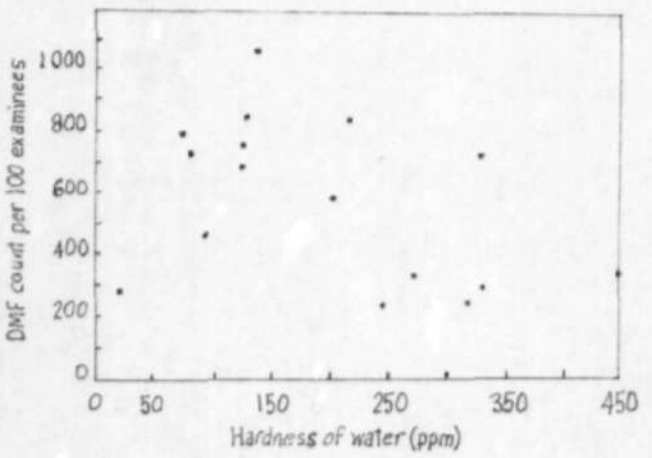


FIG. 3
RELATION BETWEEN DENTAL CARIES
& HARDNESS OF WATER



(e) First signs of excessive fluoride in drinking water are noted in the teeth but significant effects on other body tissues such as bones do not occur unless the fluoride concentration exceeds 5 ppm.

i. Effect of fluoride ingestion on caries experience.

Caries experience was expressed by the sum total of overtly carious, filled or extracted permanent teeth per person in decayed - missing - filled or caries - extractio - restauratio count. According to an investigation limited to children who were born residents of the selected districts, had always consumed the local water and in majority of whom permanent teeth and numerous teeth liable to caries had already been exposed to cariogenic influences in the oral cavity for many years, results were found as related in table 7 showing some of the cities involved.

TABLE 7: Dental Findings in Selected White School Children aged 12 to 14 Years in Relation to Fluoride Content and Total Hardness of the Public Water Supply.

City	Subjects	Fluoride mg/l	Hardness mg/l	CER/DMF 100	Molar Mortality 100	Caries	Caries-free Subjs. %
Colorado Springs	404	2.6	27	246	4.7	2.48	28.5
Elmhurst	170	1.8	323	252	11.8	4.71	25.3
Joliet	447	1.3	349	323	19.5	10.74	18.3
Aurora	633	1.2	329	281	14.5	6.16	23.5
Kewanee	123	0.9	445	343	29.3	11.38	17.9
Pueblo	614	0.6	302	412	20.2	3.75	10.6
Elgin	403	0.5	103	444	20.3	32.26	11.4
Marion	263	0.4	209	556	25.1	26.24	5.7
Lima	454	0.3	223	652	55.9	25.89	2.2
Middletown	370	0.2	329	703	65.9	55.41	1.9
Michigan City	236	0.1	141	1037	80.1	143.64	0
Oak Park	329	0.0	132	722	31.0	70.52	4.3

100 = per 100 subjects

Caries = upper incisor proximal surface caries.

The relation between caries experience and water hardness had been regarded as a determining factor in the development of dental caries.

Minor deviations from the general rule appeared in most of the fluoride tests studied indicating that caries experience is not strictly universally propotional to the fluoride content.

ii. Chronic toxic effect on enamel organ.

The influence of chronic fluorine intoxication on the structure of enamel organ during its formation is detected by the clinical appearance of the teeth. Affected teeth are characterised by minute while flecks, yellow or brown spotted areas scattered irregularly over the tooth surface and the effect is more common on permanent teeth but occurs occasionally on primary teeth.

A quantitative variation in the distribution of mottled enamel among persons using water supply containing fluoride and a quantitative diversity in the incidence among children from different endemic areas were the bases for the classification of mottling as follows:

Normal - The enamel is translucent, smooth and presents a glossy appearance.

Questionable - Occasional cases are border line between normal and very mild.

Very mild - Small, opaque, paper-white areas are seen scattered irregularly over the labial and buccal tooth surfaces.

Mild - The white opaque areas cover at least half of the tooth surface and faint brown stains are sometimes apparent.

Moderate - All tooth surfaces are involved and minute pitting is often present on the labial and buccal surfaces, brown stains are frequently a disfiguring complecation.

Moderately Severe - Pitting is marked, more frequent and generally observed on all tooth surfaces, if brown stains are present they are of greater intensity.

Severe - Affects the form of the tooth and stains are wide spread and vary in intensity from deep brown to black, the condition is sometimes referred to as corrosion type of mottling.

The differential diagnosis between mild fluorosis and non specific mottling may be difficult in individuals whose history of early fluoride ingestion is unknown.

TABLE 8: Comparison of Sound and Mottled Enamel.

	Density - gm/cc		N_2 Content - mg/gm		N_2 Content-mg/cc	
	No. of teeth	Mean ± SE	No. of teeth	Mean ± SE	No. of teeth	Mean ± SE
Sound enamel	261	2.81 ± 0.02	282	0.56 ± 0.02	243	1.59 ± 0.0
Mottled enamel	161	2.88 ± 0.02	105	0.75 ± 0.05	105	2.17 ± 0.15

The Standard Error is based on the within group standard deviation on density 0.29, nitrogen-mg/gm 0.57 and nitrogen - mg/cc 1.54.

iii. Effect of local fluoride treatment on caries experience.

Since the discovery that the fluoride ion reacts readily with calcium phosphate and apatite in the dental enamel great efforts have been made to develop efficient methods for incorporating fluoride ions into the surface of the erupted teeth by local topical fluoride applications. Some fluoride is retained after every local application depending on the concentration used. Such treatment promotes dental health primarily through its local effect upon the teeth surface and absorption of the fluoride ion. The caries protective effect varies with the method of application and factors such as post eruptive tooth age, previous cleaning and drying of teeth and supply of fluoride from other sources.

Beginning with topical application of concentrated solutions of sodium fluoride, later developments include the use of other fluoride solutions such as stannous fluoride and more elaborate methods involving the daily application of fluoride gel in a splint specially fitted to the dental arch or the use of electrophoresis to accelerate ionic movement. Simpler methods include the use of fluoride containing tooth pastes and mouthwashes. A careful, repeated manual painting of the tooth surfaces of children with 2% sodium fluoride solution reduces the caries attack by a maximum of 40% during the following year but little protection seems to be left thereafter.

Mouth washing or tooth brushing with weak solutions of sodium fluoride at intervals of two weeks or more has been reported to yield good results. The incorporation of fluoride into tooth pastes offer a daily fluoride application such that the results of a number of clinical studies conducted on different formulations of fluoride tooth pastes, generally containing 0.1% fluoride resulted in reductions of 20 to 30% in school children, higher values were reported with daily supervised brushing.

The effects and benefits of topical fluoride application in adults in areas with optimal fluoride concentration is not so far available.

D. CHRONIC TOXIC EFFECT IN THE SKELETAL SYSTEM

The chronic toxic effect of fluoride on the skeletal system has been described from certain geographical regions where drinking water contains excessive quantities of natural fluoride. This form of chronic toxic effect was first reported from India then later from Sorelenka, China, South Africa, Japan, Saudi Arabia, U.S.A., Canada and Europe. Similarly these effects were observed in relation to industrial exposure to fluorides such as cryolite.

The bone changes and skeletal abnormalities in endemic fluorisis are not as marked as those in industrial fluorisis but are similar to those seen in the heavy exposure of industrial fluorisis. The severity of the fluorisis indicated by the degree of mottling in the teeth is not proportionally reflected in the bone due to the metabolic differences of the

tissues and the different periods of development of the enamel and bone fluorisis.

The deformity and crippling fluorisis is an advanced stage of fluoride intoxication resulting from the continous exposure of an individual to 20 to 30 mg or 10.0 ppm of fluoride in the daily drinking water over a period of 10 to 20 years. There is also the additional fluoride ingestion from vegetables and foods processed in the fluoride rich water.

The crippling deformities are due partly to mechanical factors and partly to the immobilization necessitated by pain. The advanced stage of crippling fluorosis is strikingly uniform, the quadriplegic patient bent with Kyposis and restricted movement of his spine, contractures of hip and knees presents a typical result of excessive fluoride intake. Owing to the extreme fixation of the spine the body moves as a single unit with each attempt to straighten any portion of it.

E. COMMENT

Relative to the existance of fluoride in drinking water supplies and other vehicles for the ingestion of fluoride, scientific studies have brought certain findings to light.

i. Some natural fluoride ranging from less than 0.1 to 20.0 ppm is contained in all drinking waters.

ii. Foods containing varying amounts of fluoride, the highest in fish and meat, vegetables and tubers, and the lowest in citrus fruits such that the average adult ration in the U.S. contains about 0.3 mg fluorine.

iii. There are no differences in age, disease and specific mortality rates between communities having 0.7 ppm or more and comparable communities having 0.3 ppm or less of naturally occuring fluoride in the drinking water.

iv. A 10 year study of adult continous residents of a community with 8.0 ppm and a similar community with 0.3 ppm of fluoride in drinking water indicate no essential differences in medical findings.

v. The kidneys perform a rapid and efficient excretory function of water borne fluorides up to at least 5.0 ppm.

TABLE 9: A Summary of the Effects of various Doses of Fluoride Ingested through various Media on Bone, Teeth and other Organs.

Fluoride dose	Medium	Effect
1 ppm	water	Dental caries reduction
2 ppm or more	water	Mottled enamel
8 ppm	water	10% osteosclerosis
20 to 80mg/day or more	water or air	Crippling fluorsis
50 ppm	food or water	Thyroid changes
100 ppm	food or water	Growth retardation
More than 125 ppm	food or water	Kidney changes
2.5 to 5 gm	acute dose	Death

The toxic effect of larger doses of fluoride are predominantly confined to the teeth and the skeletal system with secondary involvement of the nervous system in advanced and crippling fluorisis. The skeletal changes of endemic fluorisis show irregular deposition of fluoride in bones particularly in the axial skeleton. The chemical composition of the bones is also altered and there is a marked increase of fluoride content in the bone ash. Further complications are superimposed on the skeletal lesions owing to the irregular narrowing of the spinal canal and intervertebral foramina in very advanced cases.

TESTS AND FINDINGS

1. FLUORIDE INVESTIGATION

A. INTRODUCTION

As long ago as 1892 Sir James suggested that there was some connection between fluoride in the diet and decreased liability to dental caries. He drew attention to a situation existing at North and South Shields in the U.S. with water supplies having fluoride concentrations of 0.25 and 1.4 ppm respectively stating that the amount of dental caries was 45% less with the higher concentration than with the lower.

From the first recorded investigation water supply was suspected to be the causal agent but the exact nature of the element was not discovered until 1931 when Churchill reported the presence of fluorine in water supplies in the U.S. Lantz and Smith reproduced the condition in experimental animals fed on diets containing sodium fluoride and the residue of the drinking water from an affected town. Ample evidence continues to confirm the responsibility of fluoride in drinking water for the condition in man and similar effects in the teeth of domestic animals.

Weaver in 1945 carried out an investigation in which he examined school children in North and South Shields. He also discovered that the fluorine content at North Shield was negligible but that of South Shield was 1.4 ppm and the incidence of dental caries was only 56% of that at North Shield. Thus in a period of 53 years a constant ingestion of fluoride

remains in the water supply. He concluded on further investigation in 1948 that the caries inhibitory property of fluorine is of short duration and merely postpones the development of maximum caries for about five years.

In an investigation he conducted on children of about 12 years on the effects of fluorine concentrations it was found that at a level of 1.0 ppm 10% had mottled enamel, at 2.0 ppm about 50% indicated its effect and at 5.0 ppm about 100% might be expected to have the condition with some 20% showing severe effects.

Due to investigations by Weaver the American Dental Association recommended that public water supplies should be dosed with fluorine either as sodium fluoride or sodium fluosilicate to a level of 1.0 ppm. An experiment in mass medication was started at Grand Rapids, Michigan by the U.S. Public Health Service who submitted an interim report on result as follows:

'Fluoridation of public water supply at Grand Rapids was started in Jaunary 1945 and an analysis of dental examination shows a reduced amount of dental caries experience in 1949, when compared with the pre-fluoridation rates of 1944 to 45. The findings indicated that the reduction is most pronounced in the younger group whose dentition was calcified following the addtion of 1.0 ppm of fluoride to the fluoride-free water supply.' Thus it had been established that fluoridation of water was a public health measure against dental caries.

The inhibitory property of fluorine can also be attained in three other methods:

i. The solid from administration of fluoride in tablet or other forms.

ii. The topical application of fluoride solution to teeth.

iii. The incorporation of fluoride in dentifrices.

B. DISTRIBUTION OF FLUORIDE BEARING WATERS

The relationship of fluorides to human and stock health had initiated extensive interest on the distribution of fluoride-containing waters throughout the world. Surface waters are generally low in fluoride content but underground or subsoil waters that have greater chances of contacting fluoriferous material may contain appreciable quantities depending on geological conditions. Mineral and hot spring waters are considered to have the same character as drinking water, they are however used for medical purposes.

In Africa, investigations of fluoride content of waters were carried out in South Africa, Kenya and Nigeria. In South Africa where over 300 samples from different localities were examined unusually high fluoride contents were reported as most of the region is underlain by Karoo sediments which contain about 0.5% fluoride. The levels increase during the hot and dry weather and decrease during the rainy season.

In Kenya, investigations from 850 samples gave the following results:

339 samples contain 0.1 to 0.9 ppm fluoride

146 " " 1.0 to 1.9 " "

148 " " 2.0 to 3.9 " "

12 " " 30.0 ppm and over.

The fluoride content of lakes ranged from 0.5 to 2800 ppm and of rivers and springs from 0.45 to 49.0 ppm. Many of the samples have high pH values some as high as 8 to 10. In many areas surface soils consist of high percentage of volcanic ash which pass through weathered lavas to form a water table over the impervious structures of the basement system. Chemical characteristics and climatic conditions also play an important role in the high fluoride levels.

In Nigeria, investigation on numerous samples from different locations shows that spring waters from the central plateau contain 0.2 to 0.4 ppm and in the Niger and Benue areas concentrations of up to 3.3 ppm were recorded in some places.

Investigations in South Africa were carried out by Ockerse in 1946, in Kenya by Williamson in 1953 and in Nigeria by Wison in 1954.

The U.S. Department of Health, Education and Welfare, in 1959, had provided considerable information regarding the distribution of fluoride containing waters in all the American states with respect to levels in drinking water sources. The information shows that from a total of 1903 communities, 52% were located in some five states with a fluoride content of 0.7 ppm and more and some other five indicated a fluoride level of 0.7 ppm or less. The average fluoride content in all the communities ranges from below 0.7 to 7.7 ppm.

In Chile, the northern areas have higher levels than the central or southern areas, however, the fluoride concentration ranges from less than 0.1 to 0.8 ppm.

In Cuba, samples derived from wells, aquiducts and springs indicated a fluoride concentration of 0.0 to 0.4 ppm.

In Asia, the fluoride content of waters was reported to be from below 1.0 to 20.0 ppm. From a total of about 300 samples 77% ranged from 0.1 to 1.5 ppm and the rest 23% had concentrations excelling 1.5 ppm.

In Australia, New Zealand and South Island, concentrations range from 0.0 to over 1.0 ppm with 75% of the samples within a range of 0.0 to 5.0 ppm.

In Britain, a survey of waters indicated that fluoride contents of 0.0 to 5.8 ppm exists in all drinking waters but some of the sources are either superceded or the water is mixed with low fluoride supplies.

In U.S.S.R., a total of 968 samples produced 87% with levels below 0.5 ppm, 11% of the shallow wells and 25% of artisian wells contained 0.5 to 1.0 ppm, and the rest contain levels exceeding 1.0 ppm.

TABLE 10: A Summary of Fluoride Levels in Natural Waters of some Countries.

Continent	Country	Fluoride level - ppm
Africa	Ethiopia	0.0 to 0.9
	Kenya	0.0 " 2800.0
	Nigeria	0.0 " 6.2
	South Africa	0.0 " 53.0
	Tanzania	0.0 " 95.0
America	Argentina	0.0 " 1.6
	Brazil	0.0 " 0.6
	Canada	0.0 " 1.2
	Chile	0.0 " 1.5
	Cuba	0.0 " 0.4
	Ecuador	0.0 " 1.5
	Peru	0.0 " 1.4
	U.S.A.	0.0 " 16.0
Asia	China	0.0 " 13.0
	India	0.0 " 6.4
	Iran	0.0 " 1.0
	Israel	0.3 " 1.5
	Japan	0.0 " 20.0
	Korea	0.8 " 10.0
	Taiwan	0.0 " 1.5
	Thailand	0.0 " 1.5

Table 10 (Contd.)

Continent	Country	Fluoride level - ppm		
Australasia	Australia	0.0	to	13.5
	New Zealand	0.0	"	0.9
	Papua & N.Guinea	0.0	"	0.6
Europe	Austria	0.4	"	0.8
	Czechoslovakia	0.0	"	28.0
	England	0.0	"	5.8
	France	0.0	"	7.0
	Germany	0.0	"	4.9
	Hungary	0.0	"	0.2
	Italy & Sicily	0.0	"	7.1
	Poland	0.0	"	1.1
	Spain	0.0	"	6.3
	Sweden	0.0	"	10.0

C. GEOLOGICAL ASPECTS

Fluorine is an element of igneous origin and is mostly highly concentrated in volcanic deposits. Fluorine containing minerals are widely distributed in the various sedimentary formations though few of these appear to yield significant quantities of fluorine to water. There is little information available regarding the particular geological strata responsible for the condition but in Colorado fluoride is found to be present in the surface water as in Puzzuoli, an Italian location from where imigrants showed mottled enamel as the first noted developmental defect of the teeth and has since been noted to occur endemically in America, China, Africa, India, Spain, Holland and several localised areas of England.

Other causative waters are generally reckoned to come from deep origins. In North Africa rock phosphate containing about 3.5% fluorine has been known to cause effect due to the superficial phosphatic strata contaminating soil and surface water. In Natal, South Africa the fluorine content does not exceed 0.22 ppm and no cases of dental fluorosis were reported, but in Transvaal where fluorine concentrations of 53.0 ppm are found 25% of the examined children showed mottled enamels.

The geological survey of Great Britain found that the strata which most readily yield fluorine to water are phosphatic beds and clays of marine origin such as oxford clay.

2. FLUORINE TESTS

A. INTRODUCTION

The accurate determination of fluoride in water has increased in importance with the growth of the practice of fluoridation as a public health measure. The standardisation of a constant fluoride concentration is essential in maintaining the effectiveness and safety of the fluoridation procedure. Fluorine is usually determined by matching the fading produced in a lake formed between zirconium and alizarin reactants.

Many methods for the determination of fluoride have been suggested but the colorimetric methods are most satisfactory, they are based on the reaction between fluoride and zirconium dye lake in which the fluoride reacts with the dye lake dissociating a portion of it into a colourless complex and dye. As the amount of fluoride is increased the colour produced becomes progressively lighter or different in shade depending on the reagent used.

Samples may be distilled to remove the effect of interfering ions but when the presence of such ions does not exceed the tolerable limits of the method being used fluoride determination may be made without distillation.

There are three colorimetric methods used for the determination, these are:

i. Alizarin visual method

ii. Alizarin photometric method

iii. SPADNS method.

Alizarin visual method is directly applicable to samples containing up to 1.4 mg/l but requires that the sample be used after an hour and accurate timing is not necessary as samples and standards are treated at the same time under the same condition.

Alizarin photometric method is adaptable to a greater concentration range up to 2.5 mg/l and it also requires that the sample be read at 60 $\pm$ 2 minutes.

SPADNS method does not require any waiting after the addition of reagent.

Generally, the methods are susceptible to the same interfering substances but to varying degrees, the substances which commonly cause interference are shown in table 11.

TABLE 11: Concentration of Interfering Substances causing 0.1 mg/l Error at 1.0 mg/l fluoride.

Substance	Method i		Method ii		Method iii	
	Conc. mg/l	Error	Conc. mg/l	Error	Conc. mg/l	Error
Alkalinity - $CaCo_3$	400.0	-	325.0	-	5000.0	-
Aluminium - Al^{+++}	0.25	-	0.2	-	0.1	-
Chloride - Cl^-	2000.0	-	1800.0	-	7000.0	+
Iron - Fe^{+++}	2.0	+	5.0	-	10.0	-
Hexametaphosphate - $(NaPO_3)_6$	1.0	+	1.1	+	1.0	+
Phosphate - PO_4^{---}	5.0	+	5.0	+	16.0	+
Sulphate - SO_4^{--}	300.0	+	400.0	+	200.0	+

If any one substance is present in sufficient quantity to produce an error of 0.1 mg/l or when the total interference effect is in doubt the sample should be distilled, turbid or coloured samples should also be distilled.

Appropriate precautions such as adherence to the manufacturers directions and careful calibration of the permanent standards against prepared standards must be taken in the use of permanent colour standards.

Sample dilutions or addition of appropriate quantities of interfering substances to the standards may be used to eliminate the interference effect. If alkalinity is the only interference of magnetude hydrocholric or nitric acid may be used to neutralise it and chlorine interference is removed with arsenite reagent. The volume of water sample and that of reagent added are important to the accuracy of determination, the time of reaction and the temperature are also important.

B. PRELIMINARY DISTILLATION OF WATER

1. Principle.

The direct distillation procedure do not produce dilution of the sample and using a large quantity of sample to carry out the distillation over a wide range of temperatures eliminate the need of preconcentration. The large volume of distillate and the lower starting temperature serve to hold the final sulphate concentration within tolerable limits though higher temperatures make the sulphate carry over pronounced during the later portion of distillation.

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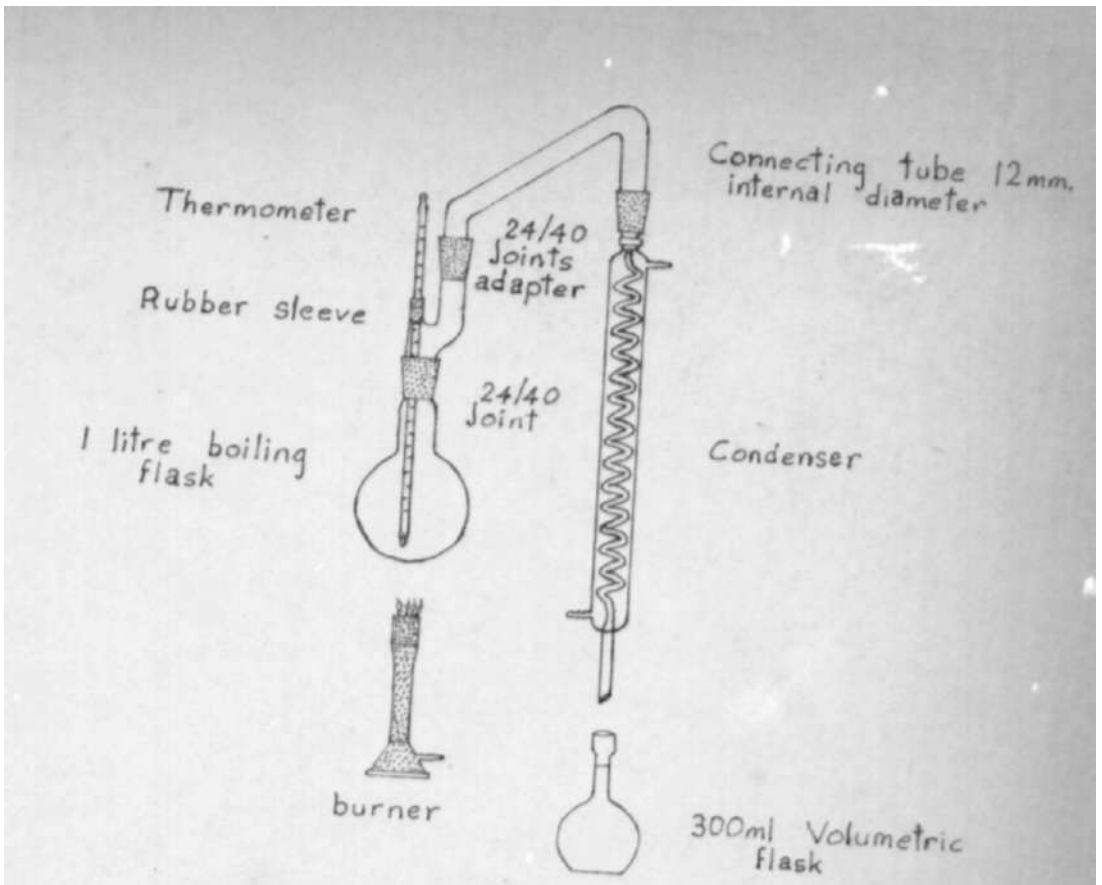


FIG. 4 DIRECT DISTILLATION APPARATUS

ii. Apparatus.

The distillation apparatus consist of:

A one litre round bottom flask

A long neck pyrex boiling flask

A thermometer adaptor

A thermometer reading to 200°C

A connecting tube

An efficient condenser.

It is important while considering apparatus to observe critically those that could effect complete fluoride recovery, and conditions which would enhance sulphate carry over.

iii. Reagents.

The reagents for this distillation are concentrated sulphuric acid and silver sulphate crystals.

iv. Procedure.

Place 400 ml distilled water in the distilling flask and carefully add 200 ml concentrated sulphuric acid and swirl carefully to obtain a homogeous solution. Add 25 to 35 glass beads, connect the apparatus and start heating making sure that all joints are tight. The heating starts slowly but increases rapidly as much as the condenser could permit until the temperature of the contents reach 180°C. The removal of fluoride contermination and adjustment of acid water ratio for subsequent distillation is more or less confined to the rapid heating so when the resulting cool distillate is discarded the removal and adjustment are believed to be accomplished.

When the remaining acid mixture is cool add 300 ml of sample and mix thoroughly; distill until the temperature reaches but not exceed 180°C so as to avoid sulphate carry over.

When high chloride samples are used add silver sulphate to the distilling flask at the rate of 5 mg per 1 mg of chloride.

The acid solution in the flask may be used repeatedly until the conterminants from the sample accumulate to a degree that recovery is affected or interferences appear in the distillate. The suitability of the acid should be periodically checked by distilling standard fluoride samples. When high fluoride samples are distilled the still should be flushed with 300 ml of distilled water before samples containing low fluoride are processed.

Fluoride recovery depends on the accuracy of the method of measurement.

C. COLORIMETRIC EQUIPMENT AND TECHNIQUE

i. Alizarin visual method

a. Apparatus.

Colour comparison equipment consists of nessleriser and match tall form nessler tubes.

b. Reagents.

The stock fluoride solution is prepared by dissolving 0.221 gm anlydrous sodium fluoride in distilled water and diluting to 1000 ml, i.e. 1.0 ml distilled water to 0.10 mg fluoride.

The standard fluoride solution is prepared by dissolving 100 ml of the stock solution to 1000 ml with distilled water i.e. 1.0 ml distilled water to 10 U gm fluoride.

Zirconyl-alizarin reagent is prepared by dissolving 0.30 gm zirconyl chloride octohydrate in 50 ml distilled water contained in a one litre volumetric flask with a glass stopper. Also dissolve 0.07 gm of 3 - alizarin sulphoric acid sodium salt in 50 ml distilled water and carefully pour into the zirconyl solution. Stir carefully and stand for sometime to clear the solution.

To prepare the mixed acid solution dilute 101 ml of concentrated hydrochloric acid to about 400 ml with distilled water, also dilute 33.3 ml of concentrated sulphuric acid to about 400 ml with distilled water. When the two are cool mix them together.

To prepare acid zirconyl-alizarin reagent add the mixed acid solution to zirconyl-alizarin reagent, add distilled water up to the mark and mix. The reagent changes in colour from red to yellow within one hour and is ready for use.

Sodium arsenite solution is prepared by dissolving 5.0 gm of the compound and diluting to 1000 ml with distilled water.

c. Procedure.

Sample treatment.

Residual chlorine is removed by the addition of 0.05 ml arsenite for each 0.1 mg chlorine and mixing.

Preparation of standards:

A series of standards are prepared by diluting various volumes of standard fluoride solution to 100 ml in nessler tubes. The standards are choosen such that some are lower and some are higher than the fluoride concentration in the sample. A standard interval of 0.05 mg/l is usually sufficient, it is

important because it determines the accuracy of determination.

Colour development.

Room temperature is satisfactory for samples and standards and should be adjusted so that the deviation between them does not exceed $2^{o}C$. Add 5.0 ml of the acid zirconyl-alizarin reagent on to 100 ml of clear sample and the standards in nessler tubes, mix thoroughly and carefully to avoid contermination during the process. After one hour compare the samples and the standards.

d. Calculations.

$$\text{mg/l fluoride} = \frac{A \times 100}{\text{ml sample}} \times \frac{B}{C}$$

where A = mg fluoride determined visually

B/C = ratio applies only when a sample is distilled to a volume B and an aliquot C taken from it for colour development.

ii. Alizarin Photometric method

a. Apparatus.

Colorimetric equipment consists of a spectrometer for use at 520 to 550 m.U providing a light path of at least 1.0 cm, or a filter photometer providing a light path of at least 1.0 cm and equipped with a green filter having a maximum transmission of 520 to 550 m U.

b. Reagent.

Standard fluoride solution.

Prepare as in - 1.

Alizarin red solution.

Dissolve 0.75 gm 3 aligarin sulphoric acid sodium salt in distilled water and dilute to 1000 ml. When insoluble materials are present they should be filtered with a filter paper and protected against sunlight.

Zirconyl acid reagent.

Dissolve 0.35 gm of zirconyl chloride octahydrate in 600 to 800 ml distilled water, slowly add 33.3 ml of concentrated sulphuric acid and 101 ml concentrated hydrochloric acid while stirring. Allow the mixture to cool to room temperature and dilute to 1000 ml with distilled water, mix thoroughly and allow to stand for one hour after which the reagent is ready for use.

c. Procedure.

Preparation of standard curve.

Prepare fluoride standards between a range 0.0 to 2.5 mg/l by diluting appropriate quantities of the standard fluoride solution to 100 ml with distilled water. Add 5.0 ml of alizarin red solution and 5.0 ml of zirconyl acid reagent to each standard, mix and allow the reaction to continue for 60 $\pm$2 minutes. Set the photometer to 0 absorbance or 100% transmittance with distilled water and take a reading on each standard using a wave length in a range of 520 to 550 m U.

Plot a curve of fluoride absorbance relationship. A new standard curve must be prepared whenever a fresh batch of either of the two reagents is prepared or when a difference standard temperature is required.

Sample pretreatment.

When residual chlorine is contained in the sample it should be removed by adding 0.05 ml of arsenite solution for each 0.1 mg of chlorine and mixing.

Colour development.

Use 100 ml of sample and adjust the temperature to that used for the standard curve. Add 5.0 ml of alizarin red solution and 5.0 ml zirconyl acid reagent and shake taking care to avoid contermination during the process. Read the absorbance after 60 $\pm$ 2 minutes setting the refrence point of the photometer as for the standard curve.

d. Calculations.

$$\text{mg/l fluoride} = \frac{A \times 100}{\text{ml sample}} \times \frac{B}{C}$$

values of A, B and C are as in - **i.**

iii. SPADNS method.

a. Principle.

The acidity of the reacting mixture greatly influence the rate of reaction between fluoride and zirconium therefore by increasing the proportion of acid in the reagents the reaction can be made practically instantaneous. Under such condition the effect of various ions differ from that in the conventional alizarin methods. The selection of dye for the rapid fluoride

method is governed largely by the resulting tolerance to these ions.

b. Apparatus.

The colorimetric equipment consists of a spectrometer for use at 570 m U providing a light path of at least 1.0 cm or a filter photometer providing a light path of at least 1.0 cm and equipped with a greenish yellow filter having maximum transmittance at 550 to 580 m U.

c. Reagents.

Standard fluoride solution.

Prepared as in - **i.**

SPADNS solution.

Dissolve 0.95 gm Spadns sodium 2 - parasulpho-phenylazo - 1, 8 - dihydroxy - 3, 6 - napthelene disulphonate, 7 - naphthelen disulphonic acid trisodium salt in distilled water and dilute to 500 ml.

Zirconyl acid reagent.

Dissolve 0.133 gm zirconyl chloride octahydrate in 25 ml distilled water, and add 350 ml concentrated hydrochloric acid and dilute to 500 ml with distilled water.

Acid zirconyl spadns reagent.

Mix equal volumes of spadns solution and zirconyl acid reagent to produce a single reagent.

Reference solution.

Add 10 ml spadns solution to 100 ml distilled water. Dilute 7.0 ml concentrated hydrochloric acid to 10 ml and add to the dilute spadns solution. The resulting solution is used

to set refrence point 0 of the spectrophotometer.

Sodium arsenite solution.

Prepared as in - **i.**

d. Procedure

Preparation of standard curve.

Fluoride standards are prepared in a range 0.0 to 1.40 mg/l by diluting appropriate quantities of the standard fluoride solution to 50 ml with distilled water. Add 5.0 ml of spadns solution and zirconyl acid reagent to each standard and mix. Set the photometer to 0 absorbance with the refrence solution and obtain the absorbance readings of the standards. Plot a curve of the fluoride - absorbance relationship and prepare a new standard curve whenever a fresh batch of reagent is made or a different standard temperature is required. Set the photometer at some suitable point established with a prepared fluoride standard if no refrence solution is used.

Sample treatment.

If residual chlorine is contained in the sample, 0.05 ml of sodium arsenite solution for each 0.1 mg chlorine is enough to remove it with thorough mixing.

Colour development.

Use 50 ml of sample and adjust the temperature to that used for the standard curve. Add 5.0 ml of spadns solution on 5.0 ml of zirconyl acid reagent and mix thoroughly. After setting the refrence point of the photometer to 0 absorbance with the refrence solution read the absorbance of the prepared solution.

e. Calculation.

$$\text{mg/l fluoride} = \frac{A \times 100}{\text{ml sample}} \times \frac{B}{C}$$

values of A, B and C are as in - i.

D. FLUORIDE LEVEL IN WATER SAMPLES EXTRACTED FROM LOCAL WELLS

i. Method of fluoride determination.

The method used in the laboratory is based on the zirconium alizarin reaction. The method which uses tablet reagents over comes all interferences except that from aluminium and high phosphate concentrations, it requires no precise control of time or temperature.

The principle of the method is based on the reaction between zirconyl chloride and sodium alizarin sulphonate in an acid solution to form a brilliant reddish violet lake. This colour is destroyed by fluoride ions to give the pale yellow colour of the alizarin sulphonate, thus varying amounts of fluoride ion produce a range of colours from yellow to red and the concentration of the fluoride can be measured by comparing the colour produced with a range of lovibond permanent colour standards.

A procedure that makes use of a prepared blank in which the fluoride has been rendered inactive by complexing it with an excess of aluminium salt is introduced so as to cancel out interference. Also, the method provides compensation for variations in reagent quality, temperature and time of colour development.

a. Reagents required.

For standard A-L procedure.

A-Z tablets - acid alizarin zirconium mixture

Excess A-L tablets - containing aluminium ammonium sulphate.

For supplementary procedure.

Resin tablets - for elimination of aluminium interference.

b. The standard lovibond nessleriser dics NOM.

Disc NOM is a wide range disc for general use in determining natural and added fluoride, it has nine standards which cover the range of 0.0 to 1.6 ppm fluoride in steps of 0.2 ppm.

c. Technique.

Standard excess A-L procedure.

Place 50 ml of sample in a nessler cylinder and add one excess A-L tablet, crush the tablet and stir until the powder is completely dissolved. Place a further 50 ml in another nessler cylinder and add one A-Z tablet to each of the two cylinders, crush and stir to dissolve the tablet. Place a further 50 ml in a third nessler cylinder and place in the left hand compartment of the nessleriser. Allow the treated samples to stand until the developed colours are both within the range of the standards in the disc, it takes 15 to 60 minutes. Place the cylinders in turn in the left hand compartment of the nessleriser and match the colour against the standards using a standard source of white light.

The difference between the fluoride readings from these two cylinders gives the fluoride content in parts per million.

Supplementary procedure.

Place 150 ml of sample in a stoppered bottle of about 250 ml capacity and add one resin tablet. Replace the stopper and disintergrate the tablet with continous shaking. Filter through a filter paper and collect two separate 50 ml portions in nessler cylinders, thereafter procede as above and if the original sample is turbid it should be filtered direct to provide 50 ml for the cylinder placed in the left hand compartment of the nessleriser.

The excess A-L technique is followed to determine total fluoride as required for fluoridation control at water works and results are for both natural and artificial fluoride. To check the fluoride dose at treatment works determine total fluoride before and after fluoridation. The difference represents artificially added fluoride. To determine free fluoride where some of the fluoride may be complexed with natural aluminium or residual alum use the excess A-L method without resin treatment, the difference between this result and the total fluoride will correspond to the complexed fluoride.

Readings obtained from the disc of a nessleriser are accurate provided that nessler cylinders which comform to the specification of those used in the original calibration are used i.e. the 50 ml calibration mark falls at a height of 113 $\pm$ 3 mm from the bottom of the cylinder measured internally.

ii. Local test results.

TABLE 12: Fluoride level in water samples extracted from local wells used by the inhabitants of villages within about five miles radius of the university campus.

Location	Source of sample	Fluoride level - ppm	Remarks
Palladan	Lined well	0.3	Used for all purposes
Unguwan-Tsofo	Unlined well	0.3	" " " "
Koraye	" "	0.2	" " " "
University Campus	Lined "	0.0	Used on mains shortage
Tudun Sarki	Unlined "	0.2	Used for all purposes
Samaru - A	Lined "	0.1	" " " "
Samaru - B	" "	0.2	" " " "
Samaru - C	" "	0.2	" " " "
Samaru - D	Unlined "	0.1	" " " "
Unguwan Na'ibi	Lined "	0.0	" " " "
Gidan Maiwada	" "	0.2	" " " "
Bomo	Unlined "	0.1	" " " "
Mil Goma	" "	0.2	" " " "
Biye	" "	0.1	" " " "
Bijimi	Lined "	0.2	" " " "
Gungurfa	Unlined "	0.1	" " " "
Birnin Bakko	" "	0.1	" " " "
Shika	" "	0.2	" " " "

The fluoride determination tests were conducted in the rainy season hence all wells were in full utility and the supply was in plenty. Public buckets were used to extract samples from the wells and sampling bottles with plastic stoppers were used to store and transport samples to the laboratory.

The samples were tested soon as they were brought to the laboratory, mostly between 10.00 a.m. and 1.00 p.m., and readings were taken at three time intervals i.e. at 30, 40 and 60 minutes ± 3 minutes for handling. No coloured samples were encountered and those that were cloudy had to be filtered to facilitate a better sight through the nessleriser. The disc NOM was used for colour comparison hence the fluoride level in the samples.

As this disc was in steps of 0.2 intermediate readings i.e. those that gave odd values, were deduced as an average of the higher and lower values corresponding to the shades of the samples and the permanent glass colour standards.

CONCLUSION

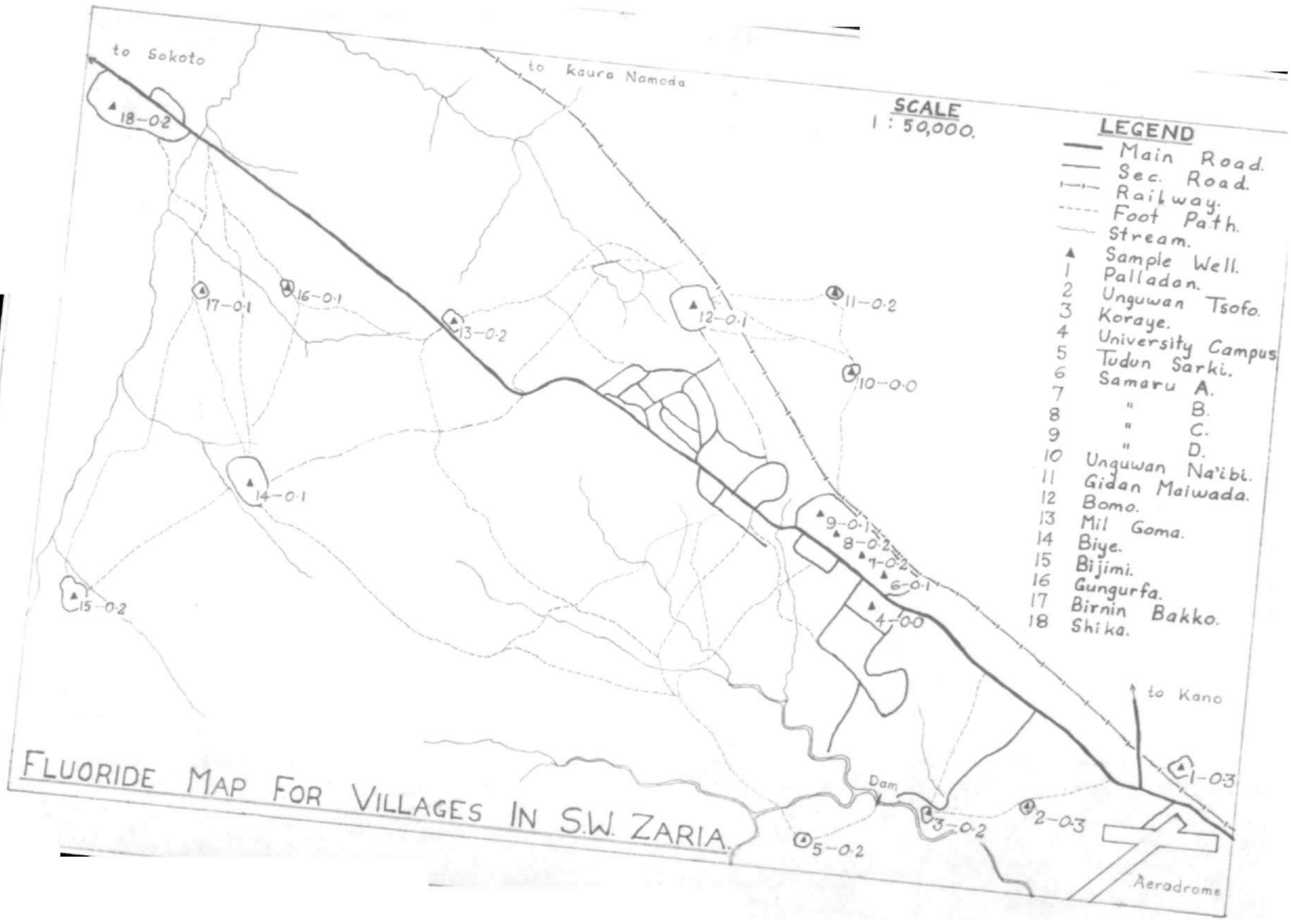
It would be observed that the flucride level in the samples tested ranged from 0.0 to 0.3 ppm, this appears to be a low concentration but with refrence to the limit within which reported tests have so far put the national level of fluoride waters to be, these results are reasonably satisfactory. The low concentration might also be attributed to the fact that the tests were carried out during the rainy season as a result of which all the wells were in full supply of water. It has been reported from almost all approved investigations that there is a relationship between the fluoride concentration in water from a supply source and the rate at which the supply is kept at any particular time i.e. concentration is proportional to the rate of supply.

From the results obtained so far it could be assumed that the strata underlying the whole area of sampling do not contain any appreciable quantities of fluoride. Out of the 18 samples tested only two which are located at one end produced levels up to 0.3 ppm, eight produced levels of 0.2 ppm, six produced levels of 0.1 ppm and only two produced levels of 0.0 ppm. Since fluoride was known to be of igneous origin the higher fluoride in those two samples might be attributed to their location in the surroundings of an igneous rock outcrop.

RECOMMENDATION

The bygone information and data on fluoridation of water relative to its stand as a public health measure have so far explained and illustrated, in factual terms, the powerful influence of the fluoride ion on the control and inhibition of dental caries. Numerous investigations, tests and experiments have come out with a number of findings that have reliably formed the bases of some universal declarations and professional recommendations regarding the addition of fluoride compounds to public water supply systems to maintain an optimal fluoride level. As a result of these researches an opinion has also been formed by the unanimous acceptance of the intake of fluoride from drinking water to play a greater role in checking the prevalence of dental caries than fluoride intake from any other source. It has been suggestively accepted that the intake of fluoride varies with the prevailing climatic conditions and environmental influences as well as the drinking habits and requirements of the individuals so that to strike at a balance of optimal intake the fluoride concentration in the drinking water has to be maintained at a minimum range of 0.7 to 1.3 ppm.

Here in Nigeria, where the climate is generally considered to be hot because it is tropically oriented the fluoride level of tested waters from general sources appears to be fairly low and on account of this dental caries experience might be substantial. It would therefore, not only be appropriate but necessary for the Nigerian authorities to introduce the process of fluoridation in all water supply systems to raise the fluoride level to a minimum of 1.0 ppm so as to combat and effectively check the growth and prevalence of the dental hazard.



FLUORIDE MAP FOR VILLAGES IN S.W. ZARIA.

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