



1936

The sorption of fluoride ion with special reference to fluoride removal from potable waters

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The Sorption of Fluoride Ion
with
Special Reference to Fluoride Removal
from
Potable Waters

A Thesis Submitted to the Graduate Committee of the
University of North Dakota in Partial Fulfillment
of the Requirements for the Degree of
Master of Science

by
Philip W. West, B. S.
//
(University of North Dakota, 1935)

Grand Forks, North Dakota

July 28, 1936

Grand Forks, North Dakota

July 28, 1936

This thesis, offered by Philip W. West as a portion of the work required for the degree of Master of Science, is hereby approved by the Committee under which he has carried on his work.

Chairman

First Minor

Second Minor

Director of the Graduate Division

Acknowledgement

The author wishes to express his gratitude to Professor G. A. Abbett for suggesting this problem and for his helpful advice and guidance throughout the investigation.

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THE SORPTION OF FLUORIDE ION

Introduction

The recent discovery that even very small concentrations of fluorides in drinking waters are sufficient to cause the serious dental dystrophy commonly known as mottled enamel, has aroused widespread interest and concern. Federal and State surveys have been conducted to determine the geographical distribution of the malady, and the fluoride contents of water supplies.

County dental surveys, conducted by the United States Public Health Department with the cooperation of local dentists, have located the regions throughout the country where mottled enamel is endemic and among these localities is an area in southeastern North Dakota and adjacent territory in South Dakota and Minnesota where domestic water supplies are obtained almost exclusively from the artesian wells of the Dakota Sandstone formation. In this district the dental lesions have been found to be especially severe.

During the past two years the writer has assisted Professor G. A. Abbott, of this University, in making a comprehensive survey of the fluoride contents of the deeper ground waters of the State with special attention to the artesian waters of the Dakota Sandstone basin. This fluoride survey was conducted in cooperation with the State Geological Survey, first, under provisions of the Federal Emergency Relief Administration and, later, with the assistance of a WPA project which is still in progress. A field survey was made by Professor Abbott in person, beginning with the counties where mottled enamel had been reported to be most severe, and later the study was extended to include practically all of the Dakota Sandstone basin in which artesian wells are found. Dentists, physicians, school administrators, well drillers, farmers, and other citizens, were interviewed, conditions were studied and numerous representative water samples were collected and returned to the University chemical laboratory for complete

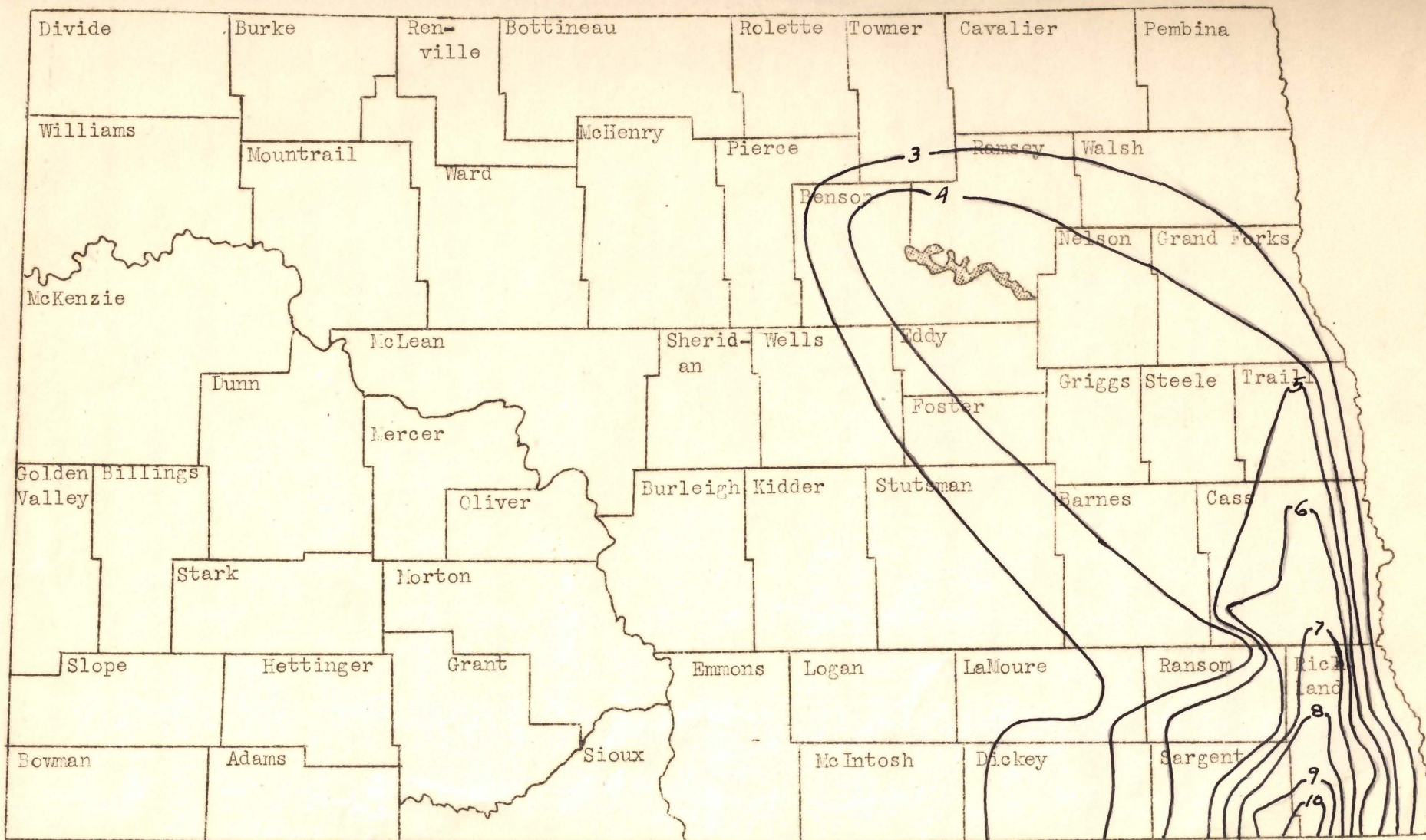
analysis. With the assistance of a specially trained competent staff these waters were then analyzed, not merely for fluorides, but for complete mineral contents, following the standards of precision of the United States Geological Survey. The writer served as assistant chemist in the FERA project, and as Supervisor of the WPA project under the direction of Professor Abbott.

The results obtained in the study of the artesian waters are interesting and surprising in that the distribution of fluorides was found to follow well defined areas or zones which could be mapped with regular contour lines enclosing the areas of different fluoride concentrations, ranging from about 3 parts per million of fluoride in the outermost zone, through successive concentric areas of increasing values, finally converging to a small district in the vicinity of Lidgerwood where the maximum value of 9.9 per million was found.

The correlation of the analytical results with the data obtained from the dental surveys was found to be complete and convincing. In every locality where the dental lesions were pronounced, the drinking waters contained notable amounts of fluorides; while in districts where fluoride-free waters are used, mottled enamel was found only among those who have moved into these districts from localities where the artesian waters are used for domestic purposes. The degree of severity of the dental lesions was found to follow the contours of the fluoride map.

The recognition of these conditions has created an insistent demand for practical methods of fluoride removal, not only for use with municipal supplies, but especially for the individual domestic supply in those regions where artesian water is the only available supply. Although considerable research on this problem is in progress, no entirely satisfactory method has been developed.

NORTH DAKOTA



AREAS OF EQUAL FLUORIDES INDICATED BY LINES
 NUMBERS REPRESENT PARTS PER MILLION OF FLUORINE

History of the Problem

In 1918 a definite relationship was noticed between the occurrence of mottled enamel and the use of certain waters for drinking purposes. Various investigators attempted to determine some constituent in the water common to the endemic areas which might cause the malady, but no progress was made until 1931 when investigators at the Arizona Agricultural Experiment Station reported that they had found fluorides present in all waters causing mottled enamel.¹

This announcement created quite a stir among chemists, dentists, and physiologists. Physiologists from various parts of the country immediately began experimenting to determine the physiological effects of fluorine. This was done mainly by feeding varied amounts of the compound to rats and dogs, noting carefully the effects produced. Chemists, on the other hand, were busy analyzing waters in order to determine which waters contained fluorine and to what extent. Using the information that was furnished by the physiologists and chemists, dentists began the work of correlating data and checking the various areas in which mottled enamel was present with the analyses of the water for that particular area. From the investigations that have been carried out it is now believed that from .8 to 1 part per million of fluoride will cause mottled enamel when consumed by children during the period when their teeth are being formed.² Animal experimentation has definitely shown that other serious effects are caused by fluorides, such as, alteration of bone structure, removal of blood calcium, hypertrophy of the thyroid gland, high blood pressure, and nervous disorders.^{3,4,5,6}

The distribution of fluorides in waters in the United States was checked by spectrographical methods by H. G. Churchill, who found that fluorine was present in Bauxite, Arkansas; Colorado Springs, Colorado; Kidder, South Dakota; Lidgerwood, North Dakota; and Oakley, Idaho. In addition to the above cities, fluorine was found to be present in Cincinnati, Ohio; Milwaukee, Wisconsin;

Birmingham, Alabama; Pittsburgh, Pennsylvania; East Saint Louis, Illinois; Kansas City, Missouri; Toledo, Ohio; Cleveland, Ohio; Detroit, Michigan; Peoria, Illinois; Indianapolis, Indiana; Buffalo, New York; Davenport, Iowa; San Francisco, California; Minneapolis, Wisconsin. Later a survey was conducted by H. T. Dean, dental surgeon of the United States Public Health Service, who found that there were 97 localities in which mottled enamel was prevalent.⁸ The principal regions on his list by states are:

- (a) Arizona. Mottled enamel is prevalent along the Gila and San Pedro rivers.
- (b) Arkansas. At Bauxite, Salem and Park counties.
- (c) California. Benton Hot Springs, Montecello, Las Legas, Elsinor Hot Springs, Warner's Ranch, north of San Diego, Maricopa.
- (d) Colorado. Colorado Springs (this is the first area in the United States where mottled enamel was reported an endemic). Powers county.
- (e) Idaho. Oakley and Casses. Also in Okyhee county.
- (f) Illinois. Miscellaneous areas using water from deep wells.
- (g) Iowa. At Ankeny.
- (h) Kansas. Reported in Chetopa, LaCrosse, Utica, and Bazine.
- (i) Minnesota. At Graceville in Big Stone county and in Traverse county.
- (j) Mississippi. At West Point, Brookville, Macon, and Montecello.
- (k) Nevada. Clark county.
- (l) New Mexico. Luna county and Grant county.
- (m) North Carolina. Horry and Beri counties.
- (n) North Dakota. At Oakes, and in Dickey, Ransom, Sargant, and Richland counties.
- (o) Oklahoma. Texas and Beaver counties.
- (p) Oregon. Opal Springs, Jefferson county.
- (q) South Carolina. Horry, Berkely and Chesleston counties.
- (r) South Dakota. Extensive throughout the state. The geological areas run into North Dakota.
- (s) Tennessee. Areas are questionable.
- (t) Texas. Widespread (northwest of Panhandle portion seems to be worse area).
- (u) Utah. Beaver county.
- (v) Virginia. Southampton counties.
- (w) Wyoming. Wright county and also in Nansemong county.

From the results of the above survey it may be seen that the distribution of fluorides is very general. More complete surveys have been made in the various states since the general survey made by H. T. Dean which will modify his report to some extent, but it has been shown that in most instances his report was generally correct.

Fluorine Discovery and History

In order to give a better understanding of the problems involved in this research a brief summary of the history, occurrence and properties of fluorine is included.

In 1529, Agricola mentioned the mineral now known as fluorite. H. Schwannhardt is reported to have etched glass by the action of sulfuric acid on fluorite as early as 1670, and G. C. Scheele in 1771 concluded that the etching was due to the formation of a peculiar acid which he called flussaurer. The isolation of fluorine was finally completed in 1886 by Henri Moisan who prepared the element by the electrolysis of a solution of potassium fluoride in anhydrous hydro-fluoric acid, using an apparatus made entirely of platinum. Fluorine generally occurs in rocks of igneous origin; for example, some of the minerals containing fluorine are: fluorite (CaF_2), cryolite (Na_3AlF_6), apatite ($(\text{CaF})\text{Ca}_4(\text{PO}_4)_3$), fluellite (AlF_3H_2), chiolite ($5\text{NaF}_3\text{AlF}_3$), sellaite (MgF_2). Fluorine also occurs in some phosphates and numerous silicates, such as, topaz, tourmaline, amphibole, lepidolite, and vesuvianite.

Properties of Fluorine

Fluorine, which is the first member of the Halogen family, is the most chemically active element known, uniting with silicon, hydrogen, carbon, and almost every other compound in the dark, except with oxygen with which it forms no compounds. It is a pale yellow gas at ordinary temperature; when liquified becomes more yellow and its solid form is pale yellow to white. The gas has a very irritating smell and acts quickly on the eyes and mucous membrane. When in contact with the skin it causes severe burns and the destruction of tissues. Inhalation either of the gas or hydrogen fluoride fumes is known to result in loss of voice and even death. Fluorides with which this problem is chiefly concerned, are

generally very stable. The fluorides of the alkaline earths are insoluble, but silver, tin, and antimony fluorides are soluble in water. The most insoluble salt being calcium fluoride.

From the observation of its properties, the problem of removal of small amounts of fluorine from water may be seen to be very difficult since it involves the removal of quantities of fluorides well below the natural solubility of fluoride bearing rocks and minerals. Thus, calcium fluoride, commonly known as fluorspar and regarded as an insoluble mineral, dissolves in water to the extent of 16 parts per million, corresponding to a concentration of about 7.8 parts per million of fluorine. When we consider that the maximum safe limit is placed at about 0.8 to 1.0 part per million of fluoride, it is clear that any effective method of removal must be able to reduce the fluoride concentration well below the natural solubilities of fluoride bearing minerals. Direct precipitation of insoluble fluorides by addition of chemical reagents seemed quite hopeless, and the only methods which held any promise of success were the physico-chemical processes involving the possible sorption of the fluoride ion upon the surfaces of active materials. Accordingly it seemed well worth while to make a systematic study of the sorption of the fluoride ion by various active absorbents in order to learn as much as possible about the process and with the hope that this information might lead to a practical method of fluoride removal.

Review of Previous Work

The Work of Boruff

C. S. Boruff of the Illinois State Water Survey reports that he has removed 5 parts per million of fluoride, which he added to the University tap water, by treatment with aluminum sulphate.⁹ His method consisted in the addition of 170 parts per million of aluminum sulphate, stirring 30 minutes, letting stand 18 to 24 hours and filtering. This reduced the fluoride to 1 part per million or less,

diminishing the amount of aluminum sulphate added, also diminished the amount of fluoride removed. Double coagulation by addition of 85 and 50 parts per million of aluminum sulphate respectively, also gave satisfactory removal. In both experiments the amount removed increased with the dosage, the optimum pH being 6.7. Boruff also reports that satisfactory removal was obtained by filtering through activated alumina or by agitation with activated alumina followed by decantation. Fresh synthetic zeolites removed fluoride but had a small capacity. Some removal resulted with co-precipitation with excess lime. He was unable to get more than a slight removal by the use of sodium aluminate, commercial bauxite, sodium silicate, silica gel, or ferric salts.

The Work of Johnston and McKee

Like Boruff, R. H. McKee and W. S. Johnston of Columbia University found that removal of fluorides by use of iron or aluminum sulphates was not practical. ¹⁰ Adsorption by the using of siliceous materials was also attempted, but gave only negative results. Sorption with carbon, however, did show some promise. Their best results were obtained by using the residual carbon of the soda-pulp industry which had been activated with acid. This activated char gave complete adsorption but only after the pH of the water had been reduced to 3 or lower.

The Work of Kramer

Fluorides were reported to have been removed by S. F. Kramer by use of a contact filter consisting of washed river sand to which had been added 2 per cent powdered aluminum metal by weight. ¹¹ It is claimed that this filter was able to remove 30 parts per million of fluoride.

Experimental

Analytical Methods Used

The validity of this research is very largely dependent upon the choice of

analytical methods used. All analyses of waters were carried out according to the procedure outlined in the Standard Methods of water Analysis, with the exception of the fluoride determination.

The quantitative estimation of fluoride in waters has been a subject of a great deal of research. Numerous methods have been proposed. The method recommended (non-standard) in the Standard Methods is the Churchill modification of the Fairchild method involving the addition of a dilute ferric chloride solution in excess of that required for the reaction: $\text{FeCl}_3 + 3\text{NaF} \rightarrow \text{FeF}_3 + 3\text{NaCl}$. The excess ferric chloride is then determined iodimetrically. A blank is run in a similar manner and the amount of excess ferric chloride found in the determination is subtracted from the excess ferric chloride determined in the blank. The difference represents the amount of ferric chloride reacting with the fluorine. This method was found to be both tedious and inaccurate, and was not considered for use. As a more suitable method which gave accurate results and at the same time is much less tedious, a modification of the Sanchis method made by Professor Abbott was chosen.¹² This method depends on the red coloration imparted to an alazarine solution upon the addition of zirconium nitrate. Zirconium nitrate reacts with fluoride to form zirconium fluoride. This latter reaction removes zirconium from the alazarine zirconium lake solution and thus causes the alazarine solution to assume its original yellow. The fading being in proportion to the amount of fluoride present. Sulphates and chlorides interfere but this is overcome by the addition of a relatively large excess of sulphate and chloride ions.

A. Detail of Abbott's Modified Method for Fluoride Determination in Waters

To 25 ml. samples in Nessler tubes, add 4 ml. 3N double acid (3N HCl mixed with 3N SO_4). Make up to 50 ml. mark with distilled water. Make up standards sodium fluoride solution and treat in the same manner as the samples. To both

the standards and the samples add exactly 1 ml. of the zirconium alazarine lake indicator. After the indicator has been added to all standards and samples, mix quickly and thoroughly by inverting the tubes a number of times. Allow the standards and samples to stand for 20 minutes at which time readings may be started. calculations: The number of mls. of standard matched $\times .1 \times 40$ gives the parts per million of fluoride.

Samples that were turbid or colored could not be determined directly by this method. The coloring could not be removed by shaking with cream of alumina because part of the fluoride would thus be removed. It was, therefore, found necessary to use the distillation method for volatilizing fluoride.

B. Distillation of Colored Samples

A sample of 100 ml. was placed in a 250 ml. distilling flask. Twenty-five ml. of concentrated sulfuric acid was added and the resultant solution brought to boiling. The initial boiling point of 110° C. quickly elevated as the solution was concentrated by distillation; when the boiling point of the solution rose to 140° C. it was held at that temperature by the addition of distilled water, which was admitted to the flask by a capillary tube extending from a separatory flask to the bottom of the distilling flask. The distillation was continued at 140° C. until 95 ml. of the distillate had been caught in a 100 ml. volumetric flask. The distillate was made up to the mark and an aliquot portion used for the determination.

To justify the choice of this method, tables are included showing the effect of interfering substances, Table I, and, also the sensitivity to known amounts of fluorides added to synthetic and natural waters, Table II. The distillation method for colored samples was also checked and is included in Table II.

Table I

Sulfates	present up to 3,000 p.p.m.	(as H ₂ SO ₄)	no interference
Chlorides	present up to 3,000 p.p.m.	(as NaCl)	No interference
Borates	present up to 5 p.p.m.		no interference
Manganese	present up to 200 p.p.m.		no interference
Silicate	present up to 50 p.p.m.		no interference
Phosphates	present up to 5 p.p.m.		no interference
Copper	present up to 5 p.p.m.		no interference
Iron	present up to 5 p.p.m.		no interference

Table II

Number of Sample	Fluoride in p.p.m.	p.p.m. of Fluoride Added	Total Fluoride Recovered	Fluoride in Original Sample After Distillation
M 190	Colored	1.2	3.8	2.6
M 197	.8	1.2	2.0	.8
M 103	.6	.8	1.4	.6
M 93	.8	1.2	2.0	.8
M 101	3.4	.4	3.6 (4)	3.4
M 86	1.2	.8	2.0	1.2
M 200	.6	.4	1.0	
M 241	3.6	1.2	4.8	

In the latter part of the research it was found that the determination of small amounts of lead was necessary. The method used was the method of Hanford and Bartow, as outlined in Standard Methods. The method was chosen because it was simple, rapid, and gave sufficiently accurate results when lead was under .3 parts per million.

Apparatus and Reagents

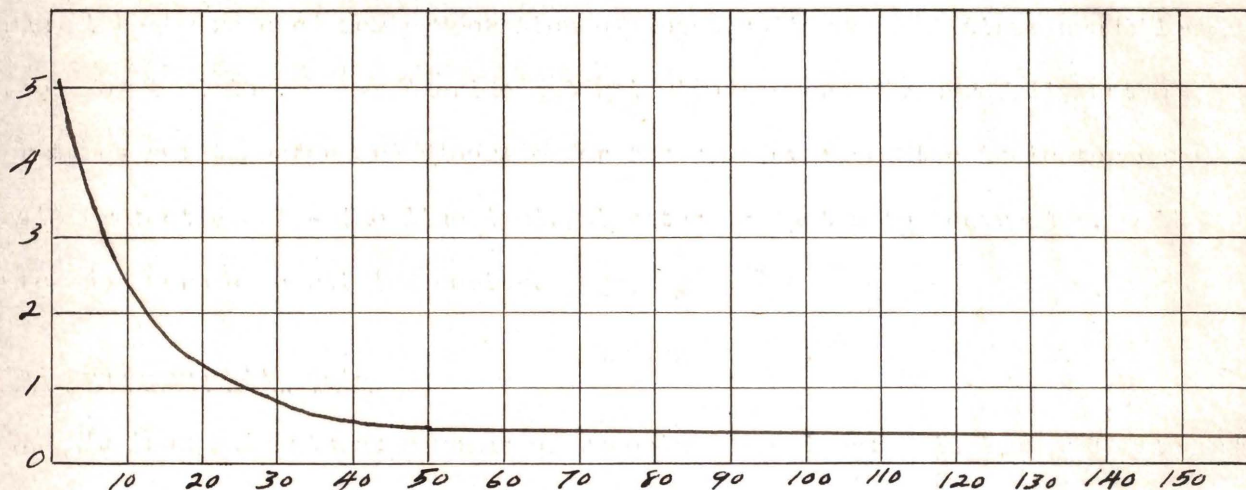
All analyses were made with apparatus as recommended in Standard Methods. Platinum dishes were used for evaporation of total solids and platinum crucibles were used for ignition. The fluoride determination was run in carefully matched Nessler tubes and the standard fluoride for the standards and the indicator were added with retested EXAX-Blue line 1 ml. pipettes graduated to hundredths. All reagents used were of certified purity.

Detailed Procedure with Data

A. Aluminum sulphate as a means of removing fluorides: Aluminum sulphate was shaken with standard fluoride water containing 5 parts per million and allowed to stand for 20 hours. The supernatant liquid was decanted and tested for removal of fluoride.

Parts per million of $\text{Al}_2(\text{SO}_4)_3$ added	Parts per million Fluoride left in Filtrate
1.0 - - - - -	5.0
5.0 - - - - -	3.0
10.0 - - - - -	3.0
15.0 - - - - -	1.5
20.0 - - - - -	1.5
30.0 - - - - -	1.0
40.0 - - - - -	0.8
50.0 - - - - -	0.4
100.0 - - - - -	0.4
150.0 - - - - -	0.4
200.0 - - - - -	0.0

P.P.M. fluoride

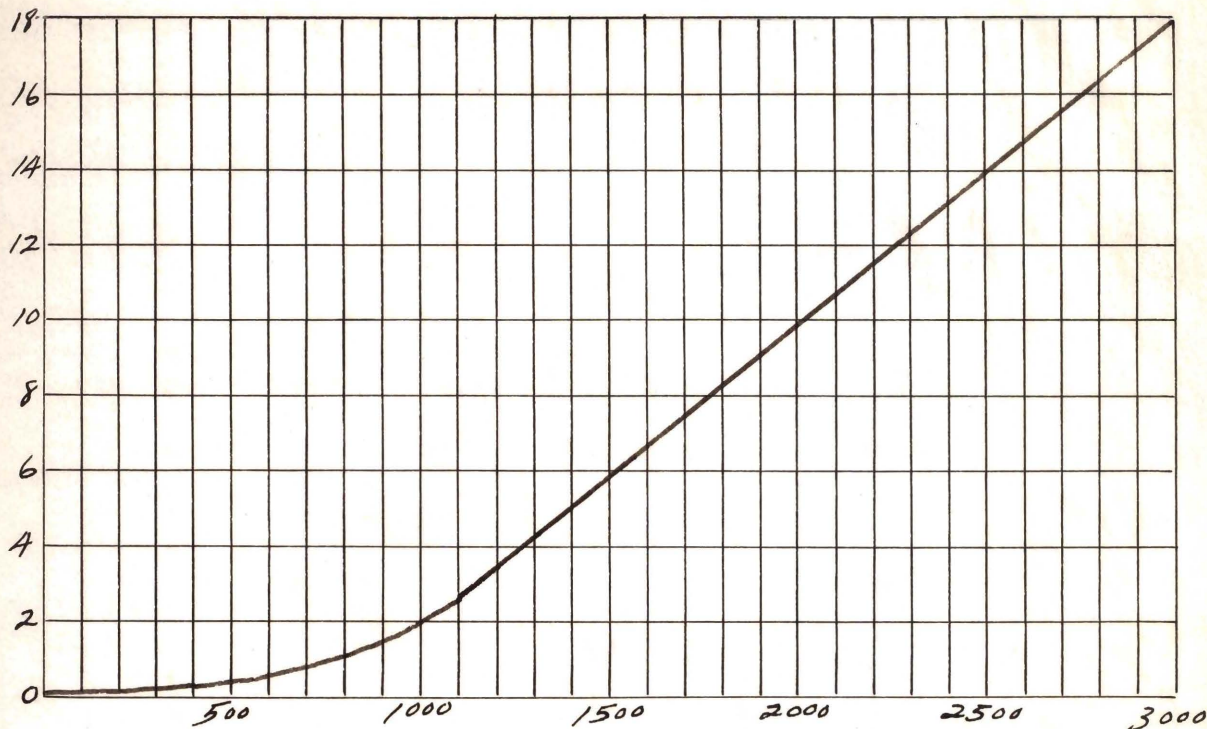


P.P.M. of aluminum sulphate

B. Artificial zeolites: Fifty grams of Professor Follin's reagent type permutit was made into a filter and charged with 10 per cent sodium chloride solution. Standard sodium fluoride water (5.0 parts per million) was poured through and the filtrate was tested for fluoride removal.

Number of ml. poured through	Parts per million remaining in filtrate
100.0	0.0
200.0	0.0
500.0	0.4
800.0	0.8
900.0	1.0
1,000.0	2.0
1,200.0	4.0
1,400.0	6.0
1,800.0	8.0
2,300.0	12.0
2,500.0	15.0
3,000.0	18.0

P.P.M. fluoride



Ml. poured through filter

Other types of zeolites, both natural and artificial have been tried with varying results, but it was found that the best results were with the reagent permutit.

C. Aluminum hydroxide: A contact filter was prepared by intimately mixing freshly precipitated aluminum hydroxide with washed lake sand. This filter removed all but 1.5 parts per million of fluoride.

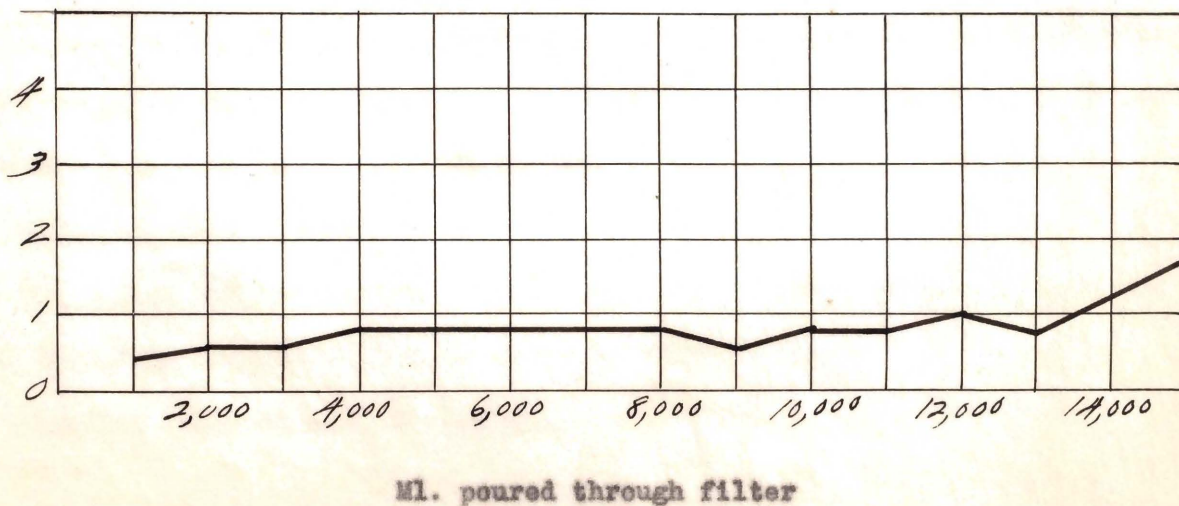
Aluminum hydroxide shaken with fluoride water and allowed to stand a few hours removed fluoride. The removal being in proportion to the amount of $\text{Al}(\text{OH})_3$ added. The amount of aluminum hydroxide necessary was too high to make this method practical.

D. Hematite: A contact filter was made with 100 grams of hematite broken

up into particles about the size of heavy gravel. A secondary filter, consisting of a layer of wood charcoal superimposed upon 50 grams of washed lake sand, was made and placed below the hematite filter to act as a clarifier. The filter was prepared by washing with 1 to 5 hydrochloric acid, followed by activation with 3 per cent ammonium hydroxide.

Number of ML. poured through	Parts per million Fluoride in Filtrate
1,000.0	0.4
2,000.0	0.6
3,000.0	0.6
4,000.0	0.8
5,000.0	0.8
6,000.0	0.8
7,000.0	0.8
8,000.0	0.8
9,000.0	0.6
10,000.0	0.8
11,000.0	0.8
12,000.0	1.0
13,000.0	0.8
14,000.0	1.0
15,000.0	1.4
16,000.0	1.6
17,000.0	1.0
18,000.0	0.4
19,000.0	0.8
20,000.0	1.0
21,000.0	1.0
22,000.0	1.0

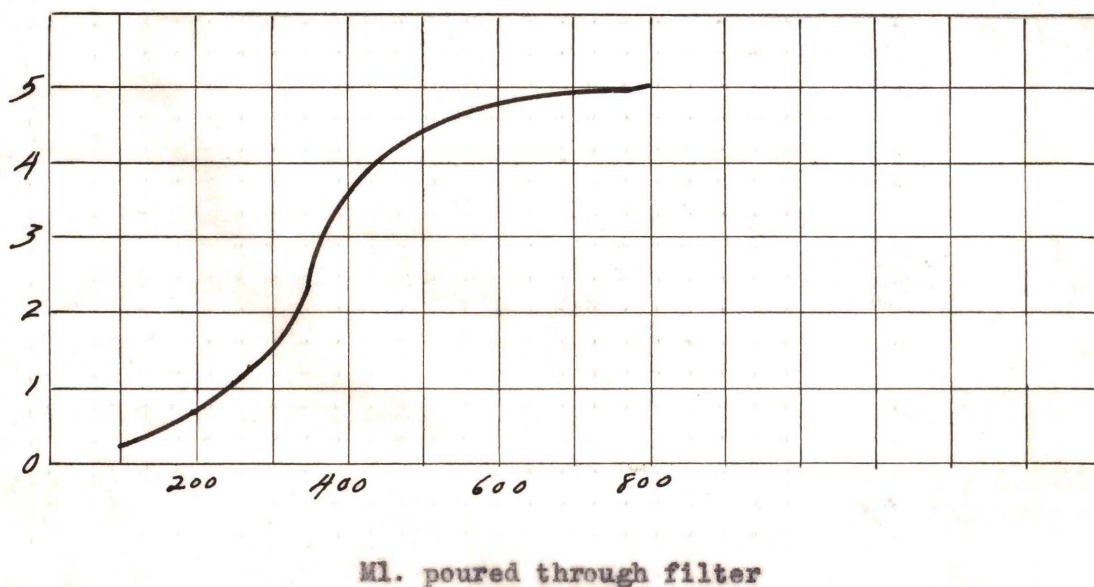
P.P.M. fluoride



E. Zircon as a means of removing fluoride: Zircon sand was placed in a bed to form a contact filter and was used as removal agent.

Number of Ml. poured through	Parts per million of Fluoride remaining in Filtrate
100.0	0.2
200.0	0.4
300.0	1.6
400.0	3.6
500.0	4.4
600.0	5.0
700.0	5.0
800.0	5.0 (4)

P.P.M. fluoride



F. Silica gel as a means of removing fluorides:

(1) Silica gel, which had been activated by moist heat for two hours under diminished pressure, was generated with 10 per cent sodium chloride. This material was then made into a contact filter.

Results: only slight removal.

(2) Silica gel was charged in a 10 per cent solution of calcium chloride, washed free from chloride and made into a contact filter.

Results: removal was only slight.

G. Specially treated zeolites:

(1) A contact filter was prepared of a zeolite. A solution of cobalt nitrate was then poured through so that the zeolite was completely charged with cobalt. A diluted solution of ammonia was then poured through and the filter washed and used as a removing agent.

Results: some removal but only a slight capacity.

(2) A second filter was prepared in the same manner as the above with the exception that nickel nitrate was used.

Results: Removal was obtained, but the capacity was so small that the method could not be considered promising.

(3) A manganese zeolite filter was prepared by treating the zeolite with manganous chloride.

Results: negative.

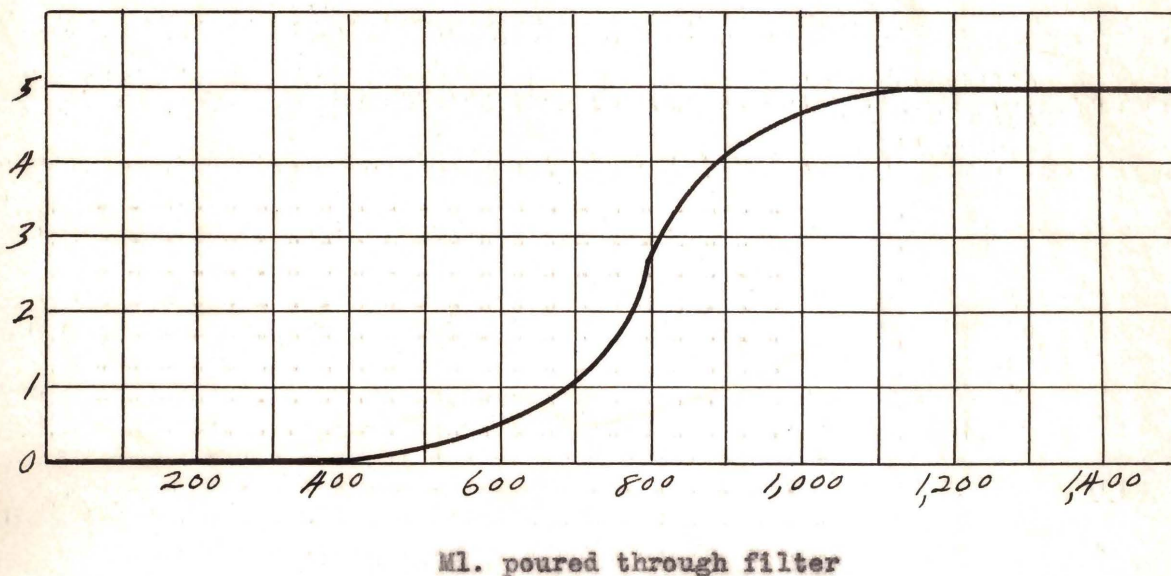
(4) Chromic chloride was placed on a zeolite filter.

Results: Fluorides were removed, but the capacity was too small to make this method practical.

(5) Zirconium nitrate was used to prepare a zirconium zeolite filter.

Number of Mls. poured through	Parts per million Fluoride in Filtrate
100	0.0
200	0.0
300	0.0
400	0.2
500	0.4
600	0.6
700	1.0
800	3.4
900	3.6
1,000	5.0
1,500	5.0

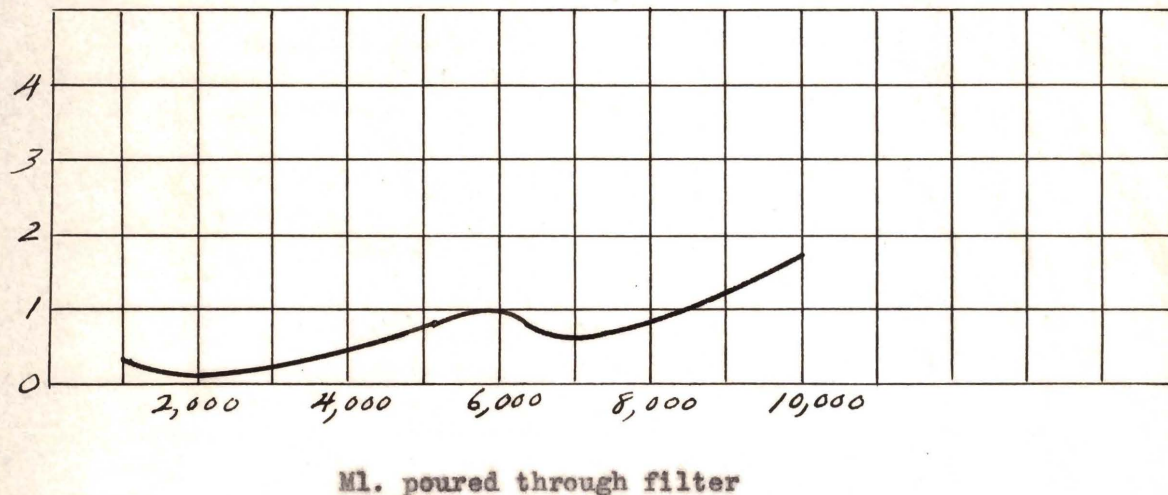
P.P.M. fluoride



(6) Ferric chloride was used to generate an iron zeolite filter. As before the hydroxide was formed on the filter by use of 3 per cent ammonia.

Number of Mls. poured through	Parts per million Fluoride remaining in Filtrate
1,000	0.4
2,000	0.1
3,000	0.2
4,000	0.3
5,000	0.6
6,000	1.0
7,000	0.6
8,000	0.8
9,000	1.2
10,000	1.6

P.P.M. fluoride



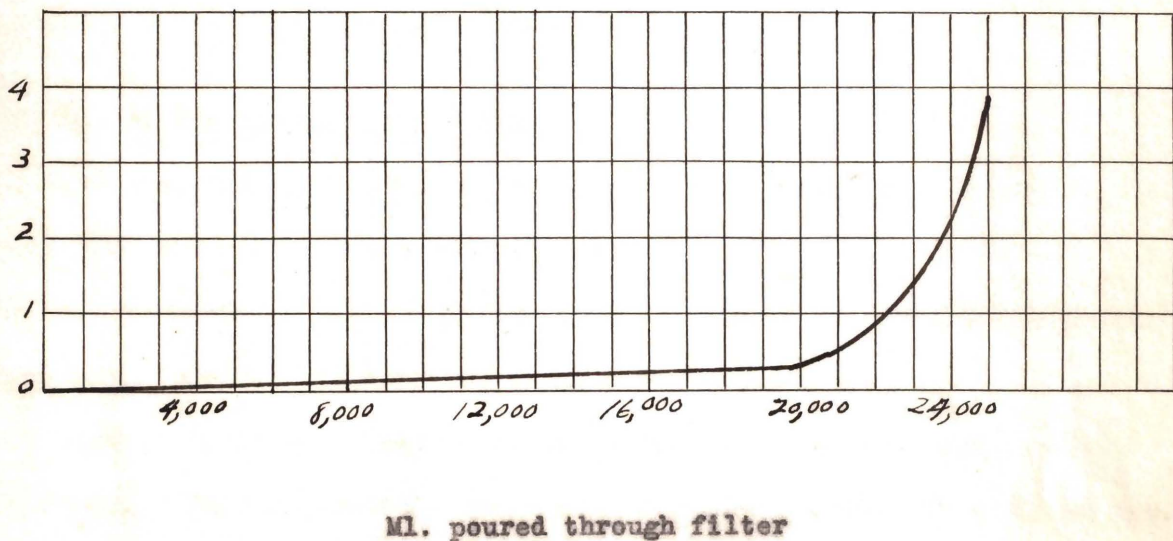
H. Carbon as a means of removing fluorides: The data of Johnston and McKee was checked and confirmed by the results obtained. A further study of sorption by use of charcoal and activated charcoal was considered inadvisable, therefore, especially since the required pH is well in the acid range which makes the method impractical.

I. Powdered aluminum metal was mixed with washed lake sand in the manner described by S. F. Kramer, but no removal was accomplished. This method was also checked independently by Hjalmer Peterson, working in this department, who also was unable to duplicate Mr. Kramer's results.

J. Zeolite plus lead chloride as a sorption agent: A filter was prepared by pouring a 10 percent solution of lead nitrate through a contact bed of zeolite. The lead zeolite thus formed was activated by use of a 10 per cent sodium chloride solution. The activation by sodium chloride resulting probably in the formation of an insoluble, basic lead chloride.

Number of Mls. poured through	Parts per million of Fluoride remaining in Filtrate
1,000	0.0
2,000	0.0
3,000	0.4
4,000	0.4
5,000	0.2
6,000	0.2
7,000	0.0
8,000	0.0
9,000	0.2
10,000	0.3
11,000	0.4
12,000	0.2
13,000	0.3
14,000	0.2
15,000	0.2
16,000	0.2
17,000	0.2
18,000	0.2
19,000	0.4
20,000	0.4
21,000	0.6
22,000	0.8
23,000	1.4
24,000	2.2
25,000	3.8

P.P.M. fluoride



Further experimentation with this type of filter has shown that it is more economical to generate the zeolite with a 2 per cent instead of a 10 per cent solution of sodium chloride as there was much less mass action on the lead by the weaker solution, and at the same time there was a sufficient amount of chloride for activation.

Another problem encountered in this method is the plumbo-solvency of certain waters. It is a well known fact that lead is a cumulative poison and that concentration of over 0.1 parts per million of lead in potable waters cannot be tolerated. It was, therefore, deemed necessary to put in a lead removing unit below the main filter. This was easily accomplished by use of a bed of zeolite which possesses a very great capacity for lead removal. It has been shown that zeolites will remove completely, approximately one and a half times their own weight of lead.¹³ By use of such a secondary filter in connection with the zeolite plus lead chloride primary filter, it was found that a fluoride-free, lead-free filtrate could be obtained.

Regeneration of the primary filter was easily accomplished by use of a 20 per cent sodium chloride solution. The secondary filter was best regenerated by using a 10 per cent sodium nitrate solution.

Interpretation of Results and Conclusions

(a) Zeolites, both artificial and synthetic, will remove fluorides, but the capacity is too small to make the method practical.

(b) Zeolites treated with manganese, nickel, zirconium, cobalt, and chromium also remove fluorides but have too small a capacity.

(c) Zeolites, used as a base on which ferric hydroxide was precipitated, gave satisfactory fluoride removal, and showed a good capacity. This method was handicapped, however, by the difficulty of preparing a filter which would give duplicate results.

(d) Activated charcoal will remove fluorides from waters after the pH has been reduced to approximately three. This method is considered impractical, being both costly and difficult to use.

(e) The 2 per cent powdered aluminum metal in sand as recommended by Kramer gave absolutely no removal, although the method was doubly checked by the author and also independently checked by Mr. Peterson.

(f) Zircon sand will remove fluoride but has slight capacity.

(g) Zeolite lead nitrate may successfully be used to remove fluoride. However, this method must be modified to include a lead removing filter. The filter thus modified could be used to do efficient work as a fluoride removing agent, but only under careful supervision and continuous checking to prevent occurrence of lead in the finished product.

This method is interesting as demonstrating that fluorides can be removed without leaving a toxic or harmful ingredient in the water; but, it is almost certain that health officials would condemn any method beginning the use of lead compounds. With competent supervision the method would be perfectly safe; but it is not "fool-proof" and in the hands of ignorant or careless attendants it might contaminate the water with lead.

Summary

1. The significance of fluorides in drinking waters is discussed from the standpoint of the occurrence of mottled enamel, particularly from the artesian waters of North Dakota.
2. Analytical methods for the determination of small concentrations of fluorides are reviewed and criticized, and a satisfactory method is described.
3. The problem of fluoride removal is discussed, and the difficulties pointed out.
4. The study of the sorption of fluoride ion on a variety of active materials is described and experimental data presented.
5. A successful method of removal is described; but one which would likely be for bidden by health authorities on account of the use of lead compounds.
6. It is suggested that the principles involved in this method might be applied to the use of some other metal of less toxic properties.
7. A Bibliography of the literature is appended.

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