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The fluorine and manganese content of certain Missouri waters

Erwin Charles Hoeman

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THE FLUORINE AND MANGANESE CONTENT OF CERTAIN MISSOURI WATERS

BY

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A

THESIS

submitted to the faculty of the
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in partial fulfillment of the work required for the
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1935

Approved by W.T. Schrenk ....
Professor of Chemistry.

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PART A

FLUORINE

INTRODUCTION

Fluorine, the most active of the elements, constitutes one tenth of one percent of the outer half-mile shell of the earth. It is the twentieth most abundant in both land and water[1]. Volcanic gases, as well as the waters of hot springs in volcanic areas, have been known to contain fluorine[2]. Although widely diffused in nature, large deposits of its minerals are of rare occurrence. Major minerals of the element are cryolite and fluorspar. It is often found associated with rock phosphates.

As early as 1850, Forchammer determined the fluorine content of sea waters, Wilson commented on its frequent presence in boiler scales, and Carles determined the concentration of the ion in mineralized waters[2].

Traces of fluorine are present, almost universally, in plant and animal tissues[1].

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1. McKay, F. S. Mottled Enamel: The Prevention of Its further Production through a Change of the Water Supply at Oakley, Ida. J. Am. Dental Assoc'n. Vol.20, p.1148 (July 1933).
2. Fitch, W. E. Mineral Waters of the United States and American Spas. New York, Lea and Febiger. p.75, (1927).

The element has been found to be a common, if not essential, constituent of bones[3].

[3] Newth, G. S. Inorganic Chemistry, 12th Ed. New York, Longmans. p.347, (1907).

Since early in 1931, considerable attention has been brought to bear upon the subject of fluorides in drinking water supplies, following the discovery of high fluoride concentrations in waters consumed by persons afflicted with the dental defect known as mottled enamel.

Analyses have been made, in the course of this study, of a comparatively large number of Missouri waters. The waters analyzed have been collected and made available by the Missouri Geological Survey and Water Resources. They have been secured from diverse sources and include surface waters and underground waters from different geological formations, throughout the State of Missouri.

Many of the waters analyzed in this study are of a highly saline type and not classed as drinking waters. Their consideration is based upon the more general purpose of showing fluorine concentration in natural waters of Missouri, and not upon the correlation with mottled enamel.

At this time of writing, no information has been found with respect to the possible presence of mottled enamel anywhere in the State of Missouri. Certain waters, used as public drinking-water supplies, have been found to contain high concentration of fluorides. It is to be hoped that communities using these supplies may be surveyed for the presence of mottled enamel. This with a view to changing the water supply, or otherwise correcting the condition.

FLUORINE AND MOTTLED ENAMEL

(a) Description of Mottled Enamel

Dean[4] describes mottled enamel as a dystrophy of the enamel, "the permanent teeth erupt, presenting a dead white or opaque appearance, sometimes being pitted. In a high percentage of cases, and in certain areas, these teeth later take on a characteristic brown stain. This developmental dystrophy is peculiar to the native-born children of an endemic area, or those taken into the area very early in childhood."

Dean[5] classifies mottled enamel diagnosis, given in abstract form in the following manner:

Normal -- The usual translucent structure, semi-vitreous in character. Enamel surface is smooth and glossy, usually of a pale creamy white color. Enamel showing hypoplasia not characteristic of mottled enamel is considered normal.

Questionable -- Aberrations of translucency ranging from scattered white flecks to occasional white spots, 1 to 2 millimetres in diameter.

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[4] Dean, H. T. Distribution of Mottled Enamel in the United States. J. Am. Dental Assoc'n. Vol.20, p.321 (Feb. 1933).

[5] Dean, H. T. Classification of Mottled Enamel Diagnosis. J. Am. Dental Assoc'n. Vol.21, pp.1421-6 (Aug. 1934).

Very Mild -- Small paper-white areas scattered or streaked over the tooth surface. Small pitted white areas are frequent.

Mild -- White opaque areas involve at least half of the tooth surface. Faint brown stains sometimes appear, most generally on the upper incisors.

Moderate -- Generally all of the tooth surface is involved. Minute pits are often present and brown stain to a disfiguring extent.

Moderately Severe -- To the eye, a greater depth of enamel appears to be involved. Smoky white appearance is often noticed, as well as pitting on all tooth surfaces. If brown stain is present, it is deeper in hue.

Severe -- The form of the teeth are at times affected. Deep and confluent pits are present. Staining is more common and ranges from chocolate-brown to black in color. This is identified with McKay's corrosion type.

According to G. V. Black[6], the cause of the injury is coincident with the absence or destruction of the cementing material between the enamel rods in the outer layers of the tooth enamel.

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6. Reed, J. J. Mottled Enamel. J. Am. Dental Assoc'n. Vol.19, p.1985 (Nov. 1932).

(b) History of Mottled Enamel

J. M. Eager[7], past Assistant Surgeon of the U. S. Public Health Service, first noticed the condition, described as mottled enamel, in the teeth of Italian emigrants coming from Pozzuoli, a community near Naples Italy. Twenty-six years later, in 1927, McKay[7] reported that a change in the water supply had prevented any new cases from occuring.

H. A. Fynn[7], of Denver, first commented on the occurence of mottled enamel in America, in a paper read before the Colorado Dental Society (1909).

In the following years, many endemic areas of mottled enamel were discovered in the United States. McKay[8], in 1925, made an examination of the teeth of school children at Oakley, Idaho. He found that every child in this community, which secured its water supply from a nearby warm spring, had a hundred percent mottling of all permanent teeth. And, on the other hand, he found that the children of a single family, dwelling near Oakley and obtaining its water supply from a different source, were entirely free of the defect.

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[7] Walker, J. S. Mottled Enamel. J. Am. Dental Assoc'n. Vol.20, p.1867 (Oct. 1933).

[8] McKay, F. S. Mottled Enamel: The Prevention of Its Further Production Through a Change of the Water Supply at Oakley, Ida. op. cit. p. 1.

Oakley changed its water supply, in consideration of this convincing evidence that something in the water was the cause of the prevalent mottled enamel. Eight years later, in 1933, McKay re-examined the teeth of children in the village who had used the new water supply during the period of their dental calcification. No new cases had developed, and cases of mild mottling, at the time of the change, had grown no worse.

The above case constitutes one of the most striking examples that a factor in the drinking water is responsible for mottled enamel.

(c) Correlation of Mottled Enamel with Fluorides in Drinking Water

H. V. Churchill[9], of the Aluminum Company of America, and Margaret Smith[10], of the University of Arizona, independently assigned the ingestion of fluorides as the specific cause for mottled enamel, early in 1931.

Churchill[9], engaged in the spectroscopic examination of waters from a deep well at Bauxite, Arkansas, noticed the presence of unsuspected quantities of fluorides. He examined waters from other endemic areas, and invariably found high fluorides concentrations.

At about the same time, Margaret Smith[10] and her co-workers at the University of Arizona, identified fluorides in the waters from the many endemic areas of that state.

Impressed with the presence of fluorides in these waters, Smith undertook a biological test of the affect of fluorides on the tooth enamel. She fed albino rats with concentrated waters from high-fluoride sources. To another set of test animals,

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[9] Churchill, H. V. Occurrence of Fluorides in Some Waters of the United States. Ind. and Eng. Chem. Vol.23, pp.996-998 (1931).

[10] Smith, M. C., Lantz, E. M. and Smith, H. V. The Cause of Mottled Enamel, a Defect of Human Teeth. Univ. of Ariz. Agri. Exp. Sta. Tech. Bul. No.32 (1931).

she fed sodium fluoride. In every instance, the young animal developed mottled enamel, or a lesion in every way identical with it.

(d) Distribution of Mottled Enamel

Instances of the enamel dystrophy have been reported in China, Spain, Mexico, Italy, Holland[11], and in the Bahama Islands, Barbados, Cape Verde Islands, and in South American countries[12].

A number of surveys have been made in this country, the most notable of which is that of Dean[13].

According to Dean's survey, the defect is particularly serious, or widespread in Arizona, in the Panhandle region of West Texas, and in an area embracing portions of the two Dakotas.

Areas of mottled enamel are reported in five of the states bordering Missouri. These are: Arkansas, Illinois, Iowa, Kansas, and Tennessee.

[11] Reed, J. J. Mottled Enamel. op. cit. p. 5

[12] Kehr, R. W. Dental Deficiencies and Drinking Water. J. Am. Water Works Assoc'n. Vol.23, p.228 (1931).

[13] Dean, H. T. The Distribution of Mottled Enamel in the United States. Public Health Rep. Vol.48, pp. 703-34 (June 1933).

He reports 97 endemic areas, occuring variously in the several states of which he makes particular mention; Arizona, Arkansas, California, Colorado, Idaho, Illinois, Iowa, Kansas, Minnesota, Mississippi, Nevada, New Mexico, North Carolina, North Dakota, Oklahoma, Oregon, South Carolina, South Dakota, Tennessee, Texas, Utah, and Virginia.

It is of interest to note that Dean's survey revealed no endemic areas in the New England states, east of the Appalachian Mountains, where Churchill[14] has reported fluorine to be absent from the water supplies. His findings with respect to the distribution of mottled enamel, widespread in the Mid-Western and Western United States, agrees with Churchill's[14] further statement that "traces at least of fluorides are to be expected west of the Appalachians."

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14. Churchill, H. V. Occurrence of Fluorides in some waters of the United States. op. cit. p. 8 .

(e) Concentration of Fluorides in Waters Causing Mottled Enamel

The concentration of fluoride which will cause mottled enamel, contradistinct from that which will not, can scarcely be stated with any great degree of exactness.

McKay[15] states, "a range from 1.0 to 13.7 parts per million in fluorine would seem to indicate a narrow margin between total immunity and a severe manifestation of this lesion, and a still more striking conjecture is that, with immunity at 1.0 part per million, there should be a typical occurrence at 2.0 parts per million, as in one known community in the West."

H. V. Smith[16] finds that concentrations as low as 0.9 parts per million of fluorine are found definitely associated with mottled enamel.

At the present stage of knowledge on the subject, any concentration of 0.9 or over parts per million of fluoride should be considered dangerous.

15. McKay, F. S. Fluorine Content of Certain Waters in Relation to the Production of Mottled Enamel. J. Am. Dental Assoc'n. Vol.19, p.1718 (Oct. 1932).

16. Smith, H. V. Determination of Fluorine in Drinking Water. Ind. & Eng. Chem., Anal. Ed. Vol.7, p.24, (Jan. 1935).

METHODS OF ANALYSIS

(a) Modern Methods

In the words of Churchill[17], "quantitative estimation of fluorides if fraught with difficulty." In his reported work, he adapted Fairchild's[18] method for fluorides in rock phosphates to the determination of fluorides in water.

After making 100 mls. of sample just acid with hydrochloric acid, he added ferric chloride solution in excess of that required to react with the fluorides present. He then added hydrochloric acid and potassium iodide, and placed the sample in a bath, held at 38° C. for one hour. The excess of ferric chloride, over that required to react with the fluorides, liberated iodine from the potassium salt. Titration of this free iodine with sodium thiosulphate solution, using starch as the indicator, served as a basis for the calculation of the fluorides present in a given sample.

[17] Churchill, H. V. Occurrence of Fluorides in Some Waters of the United States. Ind. & Eng. Chem. Vol.23, p.997, (Sept. 1931).

[18] Fairchild, J. G. Method for Determination of Fluoride in Phosphate Rock. J. Wash. Acad. of Sci. Vol.20, p.141 (1930).

Margaret Foster[19] noted factors that tended to give high results in the use of the Churchill procedure and suggested a colorimetric method[20].

The intensity of the color produced by the complex compound of potassium thiocyanate with ferric iron is less pronounced in the presence of fluoride ion. Foster compared the fading of the thiocyanate color produced by a known concentration of fluoride with that produced by the unknown concentration of fluoride in the sample.

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19. Foster, M. D. Sources of Error in the Use in Water Analysis of Fairchild's Method for the Determination of Fluoride in Phosphate Rock. Ind. & Eng. Chem., Anal. Ed. Vol.5, p.238 (1933).

20. Foster, M. D. Colorimetric Determination of Fluoride in Water Using Ferric Chloride. Ind. & Eng. Chem., Anal. Ed. Vol.5, p.234-6 (1933).

Thompson and Taylor[21] made use of the fading in color of an alizarine-zirconium lake, in the presence of fluorides, as suggested by DeBoer[22]. They found that, in the application of a colorimetric technique to original water samples, the fading rate was influenced by the presence of chloride and sulphate ions. They added sodium chloride and magnesium sulphate to the color standards used, and compensated for the effect of chloride and sulphate ions in the sample. This procedure proved entirely satisfactory in the analysis of fluoride in sea water, where the amount and ratio of chlorides and sulphates approaches a constant value. Corrections were applied to the fluoride analysis, based on the comparative chlorinity of a particular sample analyzed.

21. Thompson, T. G., and Taylor, H. J. Determination and Occurrence of Fluorides in Sea Water. Ibid. Vol.5, p.87-9 (1933).

22. DeBoer, J. H. and Basart, J. Eine schnelle massanalytische Bestimmung des Fluors auch in komplexon und unloslichen Fluoriden. Zeit. anorg. allgem. Chem. Vol.152, pp.213-20 (1926.).

Willard and Winter[23] separated fluorine from interfering ions by distilling off the fluorine "as hydrofluosilicic acid," in the presence of glass beads and perchloric acid. They titrated the distillate with thorium nitrate, using zirconium nitrate and alizarine, or alizarine alone, as the indicator.

Armstrong[24] found that the colored compound of ferric iron with acetylacetone faded to an extent proportional to the concentration of fluorides present in a sample. He applied this property of the substance to a colorimetric scheme of analysis.

Sanchis[25] modified the procedure of Thompson and Taylor[26] applying it to the determination of fluorides in waters which vary greatly in their content of chloride and sulphate ions.

[23] Willard, H. H., and Winter, O. B. Volumetric Method for Determination of Fluorine. Ind. & Eng. Chem., Anal. Ed. Vol.5, pp. 7-10 (1933).

[24] Armstrong, W. D. Colorimetric Determination of Fluorine. Ibid. Vol.5, pp. 300-2 (1933).

[25] Sanchis, J. M. Determination of Fluorides in Natural Waters. Ibid. Vol.6, pp.134-5 (1934).

[26] Thompson, T. G., and Taylor, H. J. Determination and Occurrence of Fluorides in Sea Water. Ibid. Vol.5, pp. 87-9 (1933).

He substituted hydrochloric and sulphuric acids for the salts of these acids, used by his predecessors.

Sanchis' method was used for the determinations to be reported in this writing, and shall be fully described in a later section.

(b) Comparison of Analytical Methods

The many plans of analysis, evolved within recent years, must give results which are in close agreement if they are to be used interchangeably to define toxic limits of fluoride content. This is of paramount importance in establishing a limiting fluoride content of waters used for drinking purposes.

A recent publication of H. V. Smith[27], already mentioned (p. 12), demonstrates that the methods of Foster[28], of Sanchis[29], and of Willard[30], give results which are in substantial agreement.

Smith, at the same time, found that the method of Fairchild[31], when applied to the analysis of fluorides in waters, gives results which average two to three times higher than those given by the three methods mentioned above.

27. Smith, H. V. Determination of Fluorine in Drinking Water. op. cit. p. 12.

28. Foster, M. D. Colorimetric Determination of Fluoride in Water Using Ferric Chloride. op. cit. p. 14.

29. Sanchis, J. M. Determination of Fluorides in Natural Waters. op. cit. p. 16.

30. Willard, H. H., and Winter, O. B. Volumetric Method for Determination of Fluorine. op. cit. p. 16.

31. Fairchild, J. G. Method for Determination of Fluoride in Phosphate Rock. op. cit. p. 13.

At the present time, it is highly desirable that the method of analysis be given when reporting the fluoride concentration of a water.

(c) The Application of Sanchis Method

The method of Sanchis was selected for the present work, at the suggestion of Dr. W. T. Schrenk. It was found to be well adapted to the simultaneous analysis of a large number of water samples, having a varied mineral content.

A description of the method, and of tests made to verify its accuracy and its limitations are here given.

DESCRIPTION OF SANCHIS METHOD

REAGENTS:

Standard fluoride solution -- 2.21 gms. of c.p. sodium fluoride were dissolved in distilled water to make one litre of stock solution. 10 mls. of this stock solution were diluted to one litre with distilled water, and constituted the standard fluoride solution. (Each ml. was the equivalent of 0.01 mgs. of fluorine).

Indicator -- Two solutions were made. Solution (a) contained 0.17 g. of alizarine sodium sulphonate dissolved in 100 mls. of distilled water. Solution (b) contained 0.87 g. of zirconium nitrate dissolved in 100 mls. of distilled water. Solution (a) was added to solution (b), slowly and with constant shaking. This was permitted to stand, with occasional shaking, for several hours. 20 mls. of this latter solution were diluted to

100 mls. with distilled water, and constituted the indicator solution. Hydrochloric acid (3N). Sulphuric acid (3N).

PROCEDURE:

A series of nine "standards" were prepared in 250-ml. Erlenmeyer flasks, at the time of analysis of samples. Each standard contained, respectively; 0.0, 2.5, 5.0, 7.5, 10.0, 15.0, 20.0, 25.0, and 30.0 mls. of standard fluoride solution, diluted to 100 mls. with distilled water. These standards were equivalent to the values given, in parts per million, when a 100 ml. sample of water was analyzed.

The samples for analysis were taken in 100 ml. portions when the following three conditions were present:

I. The water contained less than 500 parts per million of chloride ion.

II. The water contained less than 350 parts per million of sulphate ion.

III. The water contained less than 2.0 parts per million of fluoride ion.

When necessary, the water to be analyzed was diluted with distilled water, and 100 mls. of the diluted sample was used for the analysis.

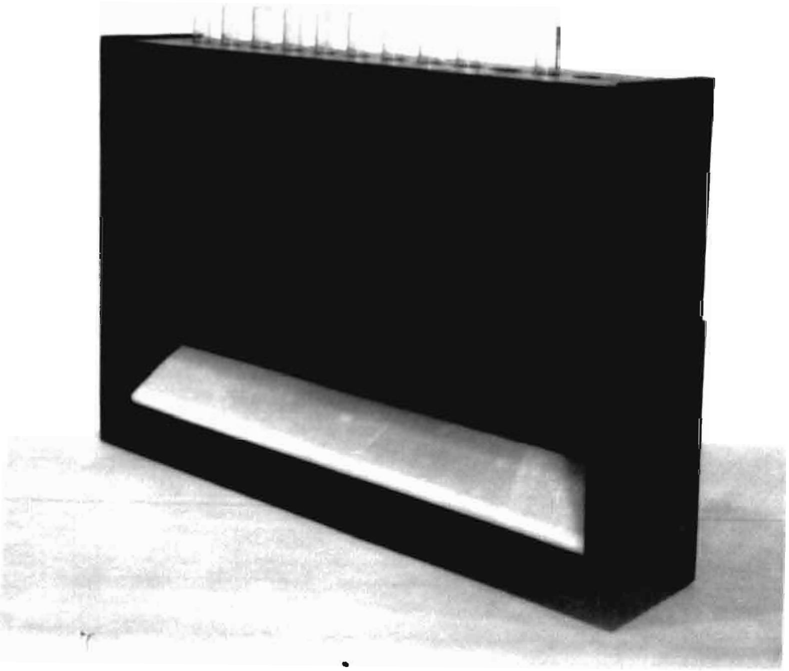
The samples were placed in 250-ml. Erlenmeyer flasks, and carried through the following details of procedure, simultaneously with the standards.

2 mls., respectively, of the hydrochloric acid, of the sulphuric acid, and of the indicator solution, were added to each sample and to each standard.

The samples and the standards were placed upon a "hot-plate", heated just to boiling, and removed from the source of heat. These were permitted to stand, at room temperature, for a period of about 12 hrs., usually over night.

The standards were transferred to 100-ml. matched Nessler tubes and made up to the mark with distilled water. Each unknown, in turn, was transferred to a 100-ml. Nessler tube, and compared with the colors of the standards.

Colors were matched by interpolation between the standards, and in a form of color comparator illustrated on the following page. In any instance where a reddish precipitate had settled in the flask, this was dissipated by swirling the contents of the flask, before transference to the Nessler tube. Colors were more distinct, and more readily matched at about 20°C. than at higher temperatures.



TESTING SANCHIS METHOD

Tests were made of Sanchis method for determining fluorides in order to determine the reproducibility of analysis and the effect of interfering ions.

Test I.

A series of synthetic waters was prepared, containing known amounts of fluorine, added as sodium fluoride. Little variation was found between "Fluorine added" and "Fluorine found." The results of this test are shown in TABLE I (p. 25).

TABLE I.

Fluorine mgs./100 mls.	Fluorine added P. P. M.	Fluorine found P. P. M.
0.01	0.1	0.1
0.02	0.2	0.2
0.04	0.4	0.4
0.06	0.6	0.6
0.08	0.8	0.75
0.10	1.0	1.0
0.12	1.2	1.2
0.14	1.4	1.4
0.16	1.6	1.6
0.18	1.8	1.8
0.22	2.2	2.2
0.24	2.4	2.4
0.26	2.6	2.6
0.28	2.8	2.6

Test II.

The original fluorine content of natural waters was determined. Known amounts of fluorine were added, and the total fluorine content of the sample was re-determined. The "Fluorine found" was substantially equal to the "Original Fluorine" plus the "Fluorine added." The results of this test appear in TABLE II.

TABLE II.

Description of Sample	Original Fluorine P.P.M.	Fluorine added P.P.M.	Fluorine found P.P.M.
Bannister, Jackson Co.	0.4	1.0	1.4
Jackson Co.	0.4	1.5	1.9
Houston, Texas Co.	0.1	2.0	2.0
Dr. Bernet, Marion Co.	2.0	1.0	2.9

Test III.

In order to test further the reproducibility of fluoride determination by Sanchis method, a series of natural waters were selected and analyzed, in duplicate. The samples selected for this study covered the range from 0.1 to approximately 5.0 parts per million.

TABLE III contains; (a) a tabulation of the duplicate analyses, with an average value of the five analyses made on each water.

Deviation of a single analysis from the average analysis is slight up to a fluoride concentration of about two parts per million. On the basis of this test, all water samples containing above two parts per million of fluoride were diluted before analysis. This is one of the three conditions necessitating dilution of the sample before analysis, as has been mentioned (p. 10).

TABLE III.

(a) Tabulation of Samples Analyzed

Location of Sample	Source*	Lab. No.	Fluorine P.P.M.
Union, Franklin Co.	S	78	0.1
Brunswick, Chariton Co.	S	47	0.3
Jefferson City, Cole Co.	S	50	0.5
Fredmar Farm, St. Louis Co.	W	102	1.0
Dr. Bernet, Marion Co.	W	26	2.2
Lake Hill, St. Louis Co.	W	99	3.0
Meyer, Cape Girardeau Co.	W	93	5.2

(b) Tabulation of Repeated Determinations

Determination	Samples						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
First	0.1	0.3	0.5	1.2	1.8	3.0	5.2
Second	0.1	0.3	0.5	1.1	2.2	3.0	5.0
Third	0.1	0.3	0.6	1.0	2.3	3.2	5.4
Fourth	0.1	0.3	0.5	1.0	2.2	2.8	5.0
Fifth	0.1	0.3	0.5	0.9	2.4	3.0	5.2
Average	0.1	0.3	0.52	1.04	2.18	3.0	5.16

* Source, S = Surface water; W = Well sample.

Test IV.

The effect of the presence of chloride on the analysis for fluorine was determined. It was found to have no more than a slight effect upon fluorine determinations when present at concentrations below 500 parts per million. This is in agreement with the findings of Sanchis[32].

When chloride ion is present at a concentration high enough to influence the determination, the apparent fluorine content is less than the actual. This appears in TABLE IV, on the following page, which shows the effect of the presence of varying concentrations of chloride ion upon the apparent concentration of fluorine.

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[32] Sanchis, J. M. Determination of Fluorides in Natural Waters. op. cit. p. 16.

TABLE IV.

Chloride Ion added P.P.M.	Actural Fluoride added P.P.M.	Apparent Fluoride present P.P.M.
50	0.5	0.5
100	0.5	0.5
150	0.5	0.5
200	0.5	0.5
250	0.5	0.5
300	0.5	0.5
350	0.5	0.5
400	0.5	0.5
450	0.5	0.5
500	0.5	0.4
600	0.5	0.3
700	0.5	0.25

Test V.

The effect of the presence of sulphate ion on the analysis for fluorine was determined. It was found to have only a slight effect upon fluorine determinations when it was present at concentrations of below 350 parts per million.

At concentrations of 350 parts per million of sulphate ion, and above, the effect of the interfering ion is to make the apparent fluorine analysis greater than the actual concentration of fluorine present in the sample.

The results of this test, showing the influence of sulphate ion upon the analysis for fluorine is given in TABLE V.

TABLE V.

Sulphate Ion added P.P.M.	Actual Fluorine added P.P.M.	Apparent Fluorine present P.P.M.
50	0.5	0.5
100	0.5	0.5
150	0.5	0.5
200	0.5	0.5
250	0.5	0.5
300	0.5	0.5
350	0.5	0.6
400	0.5	0.75
450	0.5	0.8
500	0.5	0.9
600	0.5	1.2
700	0.5	1.4

(d) Fluoride Content of Missouri Waters

The waters analyzed for fluoride content were supplied by the Missouri Geological Survey and Water Resources.

Analyses for the more commonly determined constituents of natural waters were made by Mr. R. T. Rolufs, Chemist of the Survey. These are available for reference in the files of the Survey.

TABLE VI of this thesis lists the waters analyzed in alphabetical order, according to the county of origin.

Wherever possible, the geological or surface origin of the water is given. This information, in every case, was supplied by personnel of the Survey.

Information with respect to the TREATMENT of waters, in the case of city waters supplies, was supplied by the Survey. The symbols used to represent the type of treatment are identical with those published by MISSOURI WATER AND SEWERAGE CONFERENCE, AND STATE BOARD OF HEALTH, "Key to Symbols: C -- coagulation, S -- sedimentation, F -- filtration, D -- chlorination, M -- softening, and I -- iron removal."[33]

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[33] Seventh Annual Missouri Water and Sewerage Conference. Vol. III, p. 69. (Oct. 22-3, 1931).

The content of chloride ion, sulphate ion, and the total dissolved solids of each water are tabulated with the accompanying fluoride ion content. These are included as they serve to characterize the waters to a certain extent.

Manganese and iron content of the waters are included in this tabulation (TABLE VI) as a matter of convenience, and constitute a portion of PART B of this thesis.

TABLE VI.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl*	SO_4*	DISSOLVED SOLIDS*	Mn	Fe*
Andrew	Savannah	Impounded reservoir	C.S.F.&D.	0.4	1.5	27.8	121.0	0.03	0.05
Atchison	Tarkio	210' well; water from glacial drift.		0.8	101.2	517.7	1230.0	0.03	0.07
Audrain	Mexico	1208' well; mixed water from rocks of Mississippian to Gunter age.	C.S.M.&D.	0.7	30.5	107.4	357.0	0.06	0.05
	Vandalia	1315' well; mixed waters from the St. Peter formation of Ordovician age to rocks of Cambrian age.		2.2	1352.2	364.0	3359.0	0.04	0.07
Barry	Cassville	1200' well; water from the Gunter formation of Cambrian age.		0.15				0.03	
	Exeter, St.L. & San Francisco Ry.	869' well; water from the Roubidoux formation of Ordovician age.		0.20	7.2	78.0	287.0	0.04	0.15
Barton	Lamar,	Water from a surface supply.	C.S. &D.	0.15	2.7	46.3	126.0	0.05	0.07
	Minden Mines school.	904' well; water probably from the Roubidoux formation.		2.8	52.1	44.0	910.0	0.05	0.20

* Analyses by R. T. Rolufs.

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Bates	Adrian	44' test well; water from the lower Pleasanton formation of Pennsylvanian age.		0.8	17.7	1162.1	2260.0	0.45	0.30
	G. Argenbright SE/SW 33-42-30.	402' well; water from the Bartlesville formation of Pennsylvanian age.		0.9	229.8	16.9	1036.0		0.50
	Humes-Sinclair Coal Co., SW/NE/NE. 39 N., 33 W.	1618' well; water from the Cotter formation to the Cambrian		1.6	6292.7	431.5	12844.0	0.03	0.07
	Levy Brothers, NW/NE 12-40-29.	276' well; water from the Cherokee formation of Pennsylvanian age.		1.1	116.7	737.4	1840.0	0.07	0.10
	Walter Martin, NE.$\frac{1}{4}$ 11-40-30.	436' well; water probably from the Cherokee formation of the Pennsylvanian age.		1.1	1069.4	0.25	2442.0	0.05	0.15
Benton	Warsaw	622' well; mixed water from the Cotter formation of Ordovician age to the Proctor formation of Cambrian age.		0.4	23.9	13.8	518.0	0.02	0.07

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
	Texas-Empire Pipe Line Co., 3 mi. west of Cole Camp	335' well; water from the Gasconade formation of Cambrian age.		0.6	4.5	42.2	417.0	0.04	0.05
Boone	Ashland	475' well; water from the Jefferson City formation of Ordovician age.	C.S.&D.	0.5	12.4	68.7	580.0	0.08	0.10
Cass	Belton, well #3, 14-46-33.	245' well; water from the Belton sand and the Ladore shale of Pennsylvanian age.		1.0	22.5	66.7	509.0	0.06	0.15
	Belton, well #4, 14-46-33.	245' well; water from the Belton sand and the Ladore shale.		0.4	28.4	109.3	688.0	0.16	0.80
	Kyte, NE/NW 17-46-33.	245' well; water from the Ladore shale		2.5	93.9	31.7	859.0	0.04	1.10
Cass	Myron A. King	790' well; mixed water from near base of Cherokee formation		0.7	5285.1	0.	9932.0		0.05
	Pleasant Hill	Impounded reservoir.	C.S.F.&D.	0.2	4.0	141.6	313.0	0.06	0.05
	Scott and March, SW/NE/NE 2-46-33.	820' well; water from rocks of Pennsylvanian age.		0.6	18.9	28.4	308.0	0.18	0.30

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Caldwell	Hamilton	Impounded reservoir; water from the glacial drift.	C.S.F.&D.	0.2	2.2	82.9	189.0	0.05	0.05
Camden	Camdenton	405' well; water from the Gunter formation		0.2	2.2	1.9	320.0	0.14	0.10
	Q. O. Hunter, Zebra, Mo.			0.15	6.2	10.1	430.0	0.05	0.07
Chariton	Brunswick	Water from Grand River.	C.S.F.&D.	0.3	11.9	127.4	327.0	0.01	0.05
Christian	Ozark	440' well; water from the Cotter and Jefferson City formations.		0.1				0.03	
Clay	Smithville	Platte River; water after purification.	C.S.F.&D.	0.2	6.6	177.8	371.0	0.05	0.05
Clinton	Plattsburg	River water after purification.	C.S.F.&D.	0.3	5.7	124.9	323.0	0.03	0.05
Cooper	Boonville	Missouri River water after purification.	C. S.& D.	0.4	24.7	142.8	325.0	0.03	0.07
Cole	Jefferson City,	Missouri River water after purification.	C.S.F.&D.	0.5	28.3	166.5	369.0	0.06	0.05
Crawford	Cuba,	600' well; water from the Roubidoux and Gunter formations.		0.35	3.5	18.5	270.0	0.04	0.07

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Carroll,	Carrollton	Creek water after purification.	C.S.F.&D.	0.3	7.5	46.9	253.0	0.03	0.07
Dallas,	Buffalo	662' well; water from the Gunter formation.		0.2	4.0	11.5	276.0	0.03	0.40
Dunklin,	Hornersville	Water from shallow well in the alluvium.		0.6	65.8	87.6	373.0	0.50	0.10
Franklin,	Sullivan,	825' well; water from the base of the Potosi formation of Cambrian age.		0.2	2.2	4.7	337.0	0.01	0.07
Franklin	Union,	River water after treatment.	C.S.&D.	0.10	1.8	35.8	139.0	0.03	0.10
	Washington	965' well; water from the Jefferson City and Potosi formations.		0.25	4.0	12.6	461.0	0.07	0.07
Gentry,	Stanberry,	Water from a group of shallow wells in river bottom.		0.4	109.1	558.8	1442.0	0.03	0.10
Greene,	Springfield,	Mixed water from springs river wells, and lake; after treatment.	C.S.F.&D.	0.1	4.4	12.6	234.0	0.02	0.05
	Fullbright,	Water from a spring.		0.0				0.01	

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Grundy,	Trenton,	River water after purification.	C.S.F.&D.	0.4	3.5	38.3	215.0	0.05	0.10
Harrison,	C.C.C. Camp at Eagleville.	103' well; water from the glacial drift.		0.3	10.8	204.7	686.0	0.24	0.10
	C.C.C. Camp at Eagleville.	750' well; water from the Cherokee formation.		2.4	1502.1	610.7	4150.0	0.06	0.10
	Ridgeway,	1174' well; water from the lower Cherokee formation.		2.8	1210.8	1760.2	5171.0		0.20
Harrison,	Bethany,	Water from Impounded reservoir.	C.S.F.&D.	0.3	4.9	156.8	336.0	0.03	
Henry	Clinton	River water.		0.3	20.0	91.8	290.0	0.03	0.15
	Windsor,	1117' well; water from the Cherokee formation of Pennsylvanian to the Eminence formation of Cambrian age.		0.6	5.7	60.5	358.0	0.02	0.05
Howard	Fayette,	Water from Impounded reservoir.	C.S.F.&D.	0.4	4.0	63.6	211.0	0.02	0.05
	Glasgow,	River water after purification.	C.S.F.&D.	0.6	25.2	199.4	394.0	0.08	0.07
Howell,	West Plains	Mixed waters from the Cotter formation to rocks of Pre-Cambrian age.		0.1	14.6	18.7	463.0	0.10	0.07

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
	Willow Springs,	Mixture waters from the Cotter to the Eminence formations.		0.25	3.5	3.9	257.0	0.09	0.10
Jackson	Bannister, 36-48-33.	1540' well; water from the Jefferson City formation.		0.4	22114.0	1165.0	46119.0	0.28	
	E.A. Deickman, 7909 Holmes St. Kansas City.	396' well; water from the Lexington coal horizon of Pennsylvanian age.		0.1	14936.0	0.2	33449.0	0.02	0.10
	E. Haysler, SE 5-48-33.	375' well; water from the Lexington coal horizon. Gas well, making water.		0.3	15554.0	0.0	35041.0		0.10
	Hoffman Drug Store, 45th & Main st., Kansas City.	360' well; water from the Bartlesville formation of Pennsylvanian age.		0.25	16350.0	1.0	39790.0	0.70	
	Chas. Nigro, 72nd and Grand Kansas City.	740' well; water from the Bartlesville formation.		0.25	15646.0	0.0	34536.0		4.00
	Sears, Roebuck Co. Kansas City	128' well; water from Pleistocene sediments, in abandoned valleys.		0.15	15.0	28.0	458.0	0.08	0.05
	Summe Dairy Co. Kansas City.	Water from Pleistocene sediments, in an abandoned valley.		0.10	9.7	11.5	379.0	0.03	0.05

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Jackson	Woolf Bros.Ldy. Kansas City	205' well; water from sediments of Pleistocene age.		0.15	24.7	43.4	520.0	0.06	0,05
	Malkow, 20-47-29.	505' well; water from the Cherokee formation		0.6	916.9	52.3	2324.0		0.40
	Judd Oil Co., Boten Lease NE/NW/NW. 23-48-31.	370' well; water from the Squirrel Sand of Pennsylvanian age.		0.3	7954.2	1.6	14670.0	0.03	0.40
	Judd Oil Co., Frost Lease SE/SW/NW. 22-48-32	402' well; water from Squirrel Sand.		0.25	10711.7	0.0	19413.0	0.10	0.15
	Judd Oil Co., Klopmeyer Lease near Martin City	20 to 25 wells, average depth of 350'. Producing water from the Squirrel Sand.		0.30	15130.7	3.7	29369.0	0.02	0.10
	Tribble Fee, SE/NE 30-48-32	423' well; water from the Squirrel Sand.		0.25	6610.8	0.0	12136.0	0.80	5.00
	Judd or Dallas Oil Co., Lester Lease, 6-47-33.	500 ≤ ' well; water from the Squirrel Sand. (settling tank).		0.10	15657.0	1.2	29516.0	0.10	0.07

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Jackson	Gail #2 or Elliot #2.	413' well; water from rocks of Pennsylvanian age. (gas well)		0.25	15260.5	0.0	27922.0	0.24	0.10
	F.C.McIntyre NW/SW/SW 9-48-32	314' well; water from the Peru Sand of Pennsylvanian age. (gas well)		0.20	11111.7	1.0	21100.0	0.10	0.30
	Ruff-Duck #1, 10-47-33.	357' well; water from the Peru Sand.		0.30	10787.0	0.0	20616.0	2.00	93.00
	Ruff, NE/SE 23-47-33	685' well; water from the Bartlesville Sand.		0.20	11715.9	43.6	20824.0	5.60	37.00
	Y.M.C.A., Atherton Camp 11-50-31.	322' well; water from the Lexington coal horizon.		1.2	5795.2	4.7	10576.0		0.30
Jasper	Jasper	601' well; water from the Cotter formation.		0.3	28.7	189.9	686.0	0.04	0.05
	Joplin	246 or 400' well.		0.15	8.0	135.0	508.0	0.02	0.05
	Webb City	Water from three wells, 850 to 1400' in depth. Water probably from the Roubidoux formation.		0.4	4.0	19.5	345.0	0.02	0.10

TABLE VI. Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATIONAL SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Jefferson	Eiseman # 1, SW.SW.NW. 14-42-5	450' well; water from St. Peter Sandstone of Ordovician age.		0.4	1.8	6.0	347.0	0.14	0.10
	Eiseman # 2, SE.SW.NW. 14-42-5	465 ∠ 10' well; mixed waters from the Joachim-Plattin formations of Ordovician age.		0.25	3.6	38.9	436.0	0.14	0.08
	Wm. Klein, Kimmswick, Mo.	Water from the Busberg sandstone of Mississippian age.		0.35	4.5	28.0	343.0	0.08	0.05
	Wm. Kraft SE-SE-NE- 15-41-5	780' well; water from the Roubidoux formation.		0.10	2.3	23.5	347.0	0.04	0.05
	Liberty Gun Club, Horine Missouri	Drilling well; water from the 875' level.		0.25	13.7	26.1	362.0	0.03	
	St. Lo. Lead Co., Herculaneum, Mo.	480'; well; water from the St. Peter sandstone		0.30	13.5	15.6	371.0	0.04	0.05
	St. Jo. Lead Co. Herculaneum, Mo.	1000' well; water from the Roubidoux formation		0.35	938.0	78.2	2241.0	0.05	0.07

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Johnson	Holden,	Water from impounded reservoir, after purification		0.4	3.5	33.9	188.0	0.03	0.10
	Warrensburg	1000' well; water from Jefferson City formation		0.7	104.3	37.2	495.0	0.05	0.10
Knox,	Edina,	Water from impounded reservoir, after purification	C.S.F.&D.	0.25	2.7	29.4	139.0		
	Knox City School NE-NE-SE-28-62-10	166' well; water from glacial drift		1.00	9.5	1464.1	2733.0	0.14	0.10
Lafayette,	Higginsville	Well producing from 732' to 830' depth	C.S.F.&D.	0.35	4.0	45.3	154.0	0.06	0.20
	Lexington,	Missouri River water;	C.S. & D.	0.7	30.0	182.5	489.0	0.03	0.07
	Odessa,	Impounded water	C.S.F.&D.	0.2	2.7	71.6	230.0	0.02	0.05
Lewis,	Canton,	River Water	C.S.F.&D.	0.2	7.1	56.6	213.0	0.05	0.20
	Canton O & G.Co. 14-62-6	941' well; water from the St.Peter sandstone		4.1	1831.3	1083.3	4946.0	0.06	0.10

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OF FORMATION SOURCE	TREATMENT	F	Cl	SO$_4$	DISSOLVED SOLIDS	Mn	Fe
Lewis,	W.H. Thomas, LaGrange, Mo.	Well water from the St.Peter sandstone		3.6	2928.3	1059.0	6986.0	0.05	0.05
	LaBelle, Mo.	102' well; water from the glacial drift		0.3	124.9	158.4	916.0	0.03	0.07
	G.S.Washburn, La Belle, Mo.	725' well; water from rocks of Silurian or Ordovician ages.		0.6	6.3	542.6	1303.0	0.06	0.07
	S.H.Mattingly, LaBelle, Mo.	420' well; water from rocks of Mississippian age.		0.6	17.6	242.0	729.0	0.14	0.35
Lincoln,	Prairie Pipe Line Co., Moscow Mills	740' well; water flows from St.Peter sandstone at 700'		2.2	70.8	131.6	757.0	0.03	0.15
	Troy,	325' well; water from rocks of lower Mississippian age		0.0	3.5	2.9	354.0	0.08	0.07
Linn,	Brookfield,	Water from impounded reservoir after purification.	C.S.F.&D.	0.5	4.0	59.7	201.0	0.03	0.05
	Guy Head, N orth of Browning	168' proppect hole; water from rocks of Pennsylvanian age		0.6	87.1	415.8	1254.0	0.03	0.10

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Linn,	Marceline	Water from glacial drift	C.S.M.F.&D.	0.2	3.5	35.2	162.0	0.07	0.15
Macon,	La Plata,	Water from impounded reservoir	C.S.F.&D.	0.25	2.2	49.4	163.0	0.01	0.10
	Macon,	Water from an impounded Lake	C.S.F.&D.	0.35	3.5	52.7	192.0	0.04	0.40
Marion,	A.C.Bross, W½ 17-58-5	700' well; water from St. Peter sandstone		2.4	8074.1	1184.3	17757.0	0.05	0.20
	Dr.Bernet, Hannibal,Mo.	1435' well; water from St.Peter Roubidoux formations		2.2	6047.0	1042.5	12972.0	0.04	0.05
	Palmyra,	Spring water after treatment	C.S.F.&D.	0.15	41.1	95.5	540.0	0.02	0.07
Miller,	Lakeside,	200' well; water from Gunter formation		0.15	6.2	34.4	217.0	0.07	0.20
Monroe,	Monroe City,	Lake Water	C.S.F.&D.	0.20	2.7	57.6	132.0	0.05	0.05
	Paris	Salt River water	C.S.F.&D.	0.30	4.9	131.5	275.0	0.04	0.05
Montgomery,	Wellsville,	Water from impounded reservoir		0.20	2.7	106.6	192.0	0.14	0.05
Morgan,	Versailles,	1100' well; water possibly from Potosi formation		0.30	4.0	115.8	703.0	0.05	0.10

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Nodaway,	Hopkins,	Several Shallow wells, water from glacial drift		0.3	62.3	159.7	644.0	0.12	0.10
	Maryville,	River Water	C.S.F.&D.	0.2	3.1	43.6	234.0	0.05	0.05
Oregon,	Thayer,	308' well; water possibly from Jefferson City formation		0.2	27.4	4.9	675.0	0.03	0.07
Pemiscot,	Steele,	25' wells; water from the alluvium		0.25	10.6	21.2	636.0		0.15
Perry,	Frohna Creamery Co.	505' well; water from the Plattin and Joachim formations of Ordovician age.		2.8	2.2	1072.0	1904.0	0.01	0.50
	Theo. W.Meyers, Old Appleton,Mo.	186' well; water from the Joachim formation		5.2	7.1	5.1	359.0	0.05	0.35
	Perryville,	Water from Saline Creek	C.S.F.&D.	0.2	2.2	19.1	203.0	0.03	0.10
	Wm. Ponder, C NE¼ 34-13	186' well; water from Plattin & Joachim formation		6.0	6.6	362.5	1033.0	0.07	0.20
	Theo. Tanz, SW-NE-35-34-12	498' well; water from St.Peter sandstone		0.35	28.7	37.7	642.0	0.05	0.20

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Phelps,	Rolla, School of Mines	600' well; water from Roubidoux formation to Gasconade formation of Cambrain age.		0.1	2.7	300.8	335.0	0.05	0.10
	Rolla, Mo. # 3 Mo. Gen. Utl. Co.	Water from the Potosi formation at 800'		0.25	23.4	20.6	273.0	0.02	0.07
Pike,	Bowling Green,	Water from Impounded Reservoir after purification	C.S.F.&D.	0.30	4.9	42.4	194.0	0.05	0.07
	Rob't. Burns, 16-53-1	455' well; water from St. Peter sandstone		0.6	14.1	33.9	464.0	0.14	0.07
	Clarksville,	Water from St. Peter sandstone		1.0	94.9	81.7	653.0	0.06	0.07
	Eagles Lodge, Louisiana, Mo.	1750' well; water from Roubidoux and St. Peter sandstone		3.2	45 49.0	1002.6	9575.0	0.07	0.05
	Eugene Keller, Louisiana, Mo.	720' well; water from rocks of Mississippian age to the Joachim of Ordovician age		1.1	3400.6	283.1	6986.0		0.60

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Pike,	F.H.McElroy, C 23-53-1	410' well; water from St.Peter sandstone		0.35	2.3	12.8	337	0.10	0.30
	Rob't.Mays,	413' well; water from St.Peter sandstone		0.50	2.7	27.2	348	0.50	0.07
	Ira E. Wight, SW.NE.15-52-1	316' well; water from St.Peter sandstone		0.35	5.0	26.3	414	0.03	0.05
Pettis,	Sedalia,	Lake water after purification	C.S.F.&D.	0.20	1.8	29.4	98	0.04	0.07
Platte,	Weston,	75' well; water from Missouri Valley alluvium	C.S.F.M.&I.	0.40	5.7	9.9	661	0.03	0.07
Polk,	Humansville, C.D.Thorpe	Water from flowing spring		0.25	3.1	14.4	222	0.01	0.10
Putnam,	Unionville,	Lake water		0.70	8.4	144.6	394	0.09	0.40
Ralls,	Spalding, Albert Rowland	Flowing well; water from St.Peter sandstone		2.60	5917.4	1100.1	12497		
	M.J.Jones farm, NE¼,NE¼,28-55-4	2205' well; water from Joachim formation to Pre-Cambrain		3.20	6667.2	1044.4	15385		0.25

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Randolph,	Moberly,	Lake water after Purification	C.S.F.&D.	0.3	2.7	75.1	204.0	0.03	0.05
St.Charles,	St.Charles,	Water from Missouri River	C.S.&D.	0.65	16.8	130.9	326.0	0.01	0.10
	Wentzville,	814' well; water from St.Peter sandstone		0.8	6.2	29.6	403.0	0.05	0.35
Ste. Genevieve,	Ste. Genevieve	Water from well in the alluvium		0.15	80.4	109.0	943.0	0.07	0.07
St.Louis,	Ballwin,Mo., Huber Sanitarium	200' well;water from Keokuk formation of Mississippian age.		0.3				0.01	
	Ballwin, Mo., Huber Sanitarium	800' well; water from St.Peter sandstone		1.8				0.04	
	Geo. Baumhoff, Kirkwood	957' well; water from St.Peter and Cotter formations		2.8					
	Belcher Hotel, St.Louis	2200' well; water from St. Peter sandstone		4.2				0.05	
	Desloge Farm, Hall's Ferry Rd.	1470' well; mixed waters		2.1				0.03	

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
St. Louis,	Fenton, Joseph Weil	823' well; water from St. Peter and Cotter formation		2.5	4545.7	563.5	9774.0	0.15	0.20
	Friedmar Farms Telegraph Rd.	327' well; water from rocks of Mississippian age		1.0				0.03	
	E. Kessler, NE-SE-19-44-5	215' well; water from Kimmswick formation of Ordovician age		0.1	6.8	27.0	311.0		0.07
	Kirkwood, Mo.	River water after purification.	C.S.F.&D.	0.1	7.5	17.9	147.0	0.01	0.05
	Lake Hill Near Valley Park	1800' well; water from St. Peter sandstone		3.0				0.03	
	Pond, Mo., Big Chief Hotel	429' well; water from Plattin-Joachim formations		0.15	3.2	15.4	397.0	0.04	0.07
	St. Louis, Mo.	Water from Mississippi River after purification	C.S.M.F. & D.	0.35				0.01	
	St. Louis, Mo.	Water from Mississippi before purification		0.35				0.05	

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
St. Louis	Valley Park	River water after purification	C.S.&D.	0.2	3.5	30.2	195.0	0.03	0.07
	White Mineral Springs	1190' well; water from St. Peter and Roubidoux formations		2.8				0.03	
Saline	Aldhouse NW/SE/S 28-50-21.	180' well		2.1	478.0	92.4	1428.0	0.06	0.30
	Bomhake, NE/SE/ 17-50-21.	90-100' well; water from the glacial drift		0.3	8.4	75.9	276.0	0.07	0.20
	L. Black NE/NE/ 29-49-19.	296' well; water probably from rocks of Mississippian age.		0.9	396.8	92.2	1171.0	0.04	0.10
	S. H. Black, 7 miles West of Slater, Mo.	606' well; water from the Burlington formation		0.0	9.8	30.9	640.0		0.10
	Blosser et. al., NE/NE-20-50-21	1425' well; water from rocks of Cambrian age.		0.65	1903.1	0.0	4287.0	0.04	0.80

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Saline	Brown, SE-NE-SW 7-50-20	112' well; water from rocks of Pennsylvanian or Mississippian age		0.35				0.08	
	F. Brown, NE-NW-SW 9-50-20	157' well; water from the glacial drift		0.2	3.2	10.9	347.0	0.18	0.07
	T. J. Davis, NW-SE-SE. 20-50-19	298' well; water from rocks of Mississippian age.		0.6	80.3	41.6	567.0	0.01	0.07
	T. E. Embry, SW-NW-SW. 16-50-19	351' well; water from rocks of Mississippian age		0.4	3.2	27.8	373.0	0.04	0.10
	W. Fields, SE-NW-NW 34-52-20	600'-700' well; water from Jefferson City formation		1.0	3.6	47.5	470.0	0.06	0.15
	P. Fulkerson, SW-NW-SW 29-50-22	510' well; water from the St. Peter sandstone		0.75	19.4	42.4	627.0	0.01	0.30
	H. A. Gregor, SE-SW 7-50-19	427' well; water from rocks of Mississippian age.		0.7	3.2	16.7	340.0	0.02	0.10
	I. W. Griffis, Nelson, Missouri.	334' well; water probably from the St. Peter sandstone.		2.8	2146.6	244.2	4721.0	0.03	0.15
	M. Hardin, SE-SE 17-52-20	100±' well		0.55	261.6	67.3	837.0	0.06	0.35

TABLE VI. Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Saline	Hite, NE/NW/SW 3-50-21	255' well; water probably from the Cherokee formation		0.9	2342.1	301.2	5114.0	0.32	0.50
	H. H. Hyland, NE/SE 34-50-21	460' well; water from rocks of Mississippian age		1.5	19.8	51.4	614.0	0.03	0.35
	Chris. John, NE/NW/NW 1-49-22	575' well; water from rocks of Mississippian age or the St. Peter sandstone		2.6	712.5	59.3	1641.0	0.06	0.20
	Frank Lawless, NE/NE/SW 23-50-20	260' well; water from rocks of Mississippian age		0.35	28.9	19.1	414.0	0.80	0.30
	B. Leimkuehler, NE/NW 17-50-19	232' well; water from rocks of Mississippian age		0.6	6.3	55.8	451.0	0.03	0.30
	McAllister, SW/NW 34-48-22	496' well; water from rocks of Mississippian age		0.8	230.4	110.7	1067.0	0.02	0.10
	Marshal, Mo.	130' well; water from glacial drift		0.35	157.3	42.0	634.0	0.08	0.50
	Marshal Ice Co.	130' well; water from the Cherokee formation		0.40	609.8	89.9	1537.0	0.10	0.20

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Saline,	Mo.School for Feeble Minded, NE-NE-11-50-21	231' well; water from Cherokee formation		0.5	176.8	183.5	778.0	0.08	0.10
	L.M.O'Dell, NE-SE-19-50-19	265' well; water from rocks of Mississippi or Pennsylvanian age		0.6	3.6	23.2	451.0	0.03	0.35
	Page Milk Co., SW-NW-15-50-21	135' well; water from glacial drift		0.4	11.0	22.0	342.0	0.18	0.20
	Reynolds, NE-NE-4-50-21	110' well; water from glacial drift		0.45	7.5	9.9	186.0		
	J.J.Robertson NW-SE-11-50-23	480' well; water from rocks of Mississippian age or from the St. Peter sandstone		0.40	0.5	8.6	248.0	0.02	0.10
	Saline Oil Co., NE-SE-NE-19-51-22	1250' well; water flowing from Roubidoux, Gasconade and lower formations		3.00	8505.1	1468.2	18262.0	0.14	0.25

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Saline,	Slater, Mo.	River water		0.2	12.8	50.4	266.0	0.03	0.10
	L. Smith, NE/SW/SW 28-52-20	439' well; water probably from the St. Peter sandstone.		0.85	22.1	59.3	503.0	0.06	0.12
	Sweet Springs, Mo.	600' well; water from the Burlington to Cotter formations.		1.2	892.6	65.6	2219.0	0.02	0.10
	Noland Taylor, NE/NW 29-49-19	351' well; water probably from the St. Peter sandstone		1.3	2354.0	274.1	5286.0		0.35
	Zahn, SE/SW/NE. 9-50-21.	107' well; water from glacial drift.		0.35	7.1	34.8	264.0	0.04	0.05
	Zahn, SE/SW/NW. 9-50-21.	231' well; water from the Cherokee formation.		2.2	2412.8	377.8	5227.0	0.05	0.10
Schuyler,	Lancaster, Mo. School.	30' well; water from the glacial drift.		0.85	10.8	281.7	775.0	0.03	0.07
	Lancaster School E.R.A. Well.	257' well; water from the glacial drift.		0.80	32.5	1541.3	2629.0	0.04	0.05
	Lancaster; North side of Courthouse	47' well; water from the glacial drift.		0.30	460.0	354.5	2042.0	0.04	0.60

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OF FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Taney	Forsyth, Mo. Consolidated school.	Well water from the Roubidoux formation		0.1	2.7	7.4	282.0	0.03	0.20
	Rockaway Beach	425' well; water from the Jefferson City and Roubidoux		0.25	3.1	11.9	458.0	0.02	0.07
Texas	Houston, Mo. 5-30-9	700' well; water from the Gasconade and Gunter formations		0.10	3.6	4.1	288.0		0.07
Vernon	Mrs. Falor, NE$\frac{1}{4}$ NE$\frac{1}{4}$ 29-38-32	813' well; water from the Bartlesville to St. Peter sandstone		1.0	742.4	75.5	1787.0		0.15
	Horton Gun Club, 22-37-41	817' well		1.0	583.3	69.1	1373.0	0.04	0.10
	Nevada O. & G. Co. near Rinehart, Missouri	2018' well		0.8				0.12	
Warren	Warrenton, Mo.	900' well; water from the Jefferson City and Roubidoux formation		1.4	37.6	66.3	444.0		0.10

TABLE VI. CONT'D.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
	W. A. Pruner, NE/SE 29-66-14.	260' well; water from the glacial drift		0.35	178.6	155.5	1404.0	0.05	0.05
Scott	Benton, Mo.	1500' well; water probably from the Cotter formation		0.20	25.6	10.9	388.0	0.03	0.05
	Illmo, Mo.	921' well; water from the St. Peter sandstone.		0.25	4.0	8.8	332.0	0.18	0.05
	Sikeston, Mo.	412' well; water from the alluvium.		0.30	6.6	1.0	173.0	0.14	0.05
Shelby,	Shelbina, Mo.	Water from Salt River	C.S.F.&D.	0.70	3.1	85.4	196.0	0.06	0.10
Sullivan	Milan, Mo.	Water probably from the city lake	C.S.F.&D.	0.40	5.3	114.6	289.0	0.06	0.50

TABLE VI Cont'd.

COUNTY	LOCATION	ORIGIN OR FORMATION SOURCE	TREATMENT	F	Cl	SO_4	DISSOLVED SOLIDS	Mn	Fe
Worth,	Grant City,	35' well; water from glacial drift		0.4	6.6	38.5	254.0		0.10
Wright,	Mansefield,	615' well; water from the Roubidoux and Eminence formations		0.2	6.2	16.3	298.0	0.01	0.25

DISCUSSION OF FLUORINE IN MISSOURI WATERS

(a) Source of Water with Relation to Its Fluorine Content

All of the waters that were obtained from surface supplies, and from unconsolidated and recent geological formations, were comparatively low in fluorine content. Seventy one waters of this type were analyzed with the results as are shown in TABLE VII (p. 62).

Thirty two waters of formations of Pennsylvanian Age were analyzed for fluorine content. This group of waters varied in fluorine concentration between the limits of 0.1 and 2.8 parts per million. Twenty two waters of this origin were from wells in middle western Missouri (Jackson, Cass, Bates, and Vernon Counties) and, in many instances, were obtained from formations associated with the occurrence of oil and gas.[34] Fourteen waters from oil and gas formations, in Jackson County, were of comparatively low fluorine content -- from 0.1 to 0.4 parts per million. Waters from similar formational sources, in the southern counties of this area (Cass, Bates, and Vernon), ranged in fluorine content from 0.6 to 2.5 parts per million. Two waters from the Cherokee formation of Pennsylvanian Age, in

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34. F. C. Greene: Biennial Report of the State Geologist (Missouri), Appendix II, p. 5 (1933).

TABLE VII.

	Number of Samples	Fluorine Content in P.P.M.		
		Highest	Lowest	Average
Impounded Reservoirs	12	0.5	0.2	0.31
Lakes	6	0.7	0.1	0.30
Rivers and Streams	24	0.7	0.1	0.33
Springs	3	0.25	0.1	
Alluvial Deposits	7	0.6	0.1	0.33
Glacial Drift	19	0.85	0.1	0.37
All Surface Supplies and Unconsolidated Formations	71	0.85	0.1	0.31

Harrison County (north central Missouri) had fluorine concentrations of 2.4 and 2.8 parts per million, respectively.

Boruff and Abbott[35] report fluorides in waters obtained from formations of Pennsylvanian Age, in Illinois.

Twelve waters were obtained from formations of Mississippian Age. The fluorine content of these varied from 0 to 1.5 parts per million. It is worthy of note that waters from the Mississippian rocks, in southeastern Kansas have been responsible for severe mottling of the enamel. Kehr[36] says, "The Chetopa district, a known endemic area, was reported from Coffeyville, Oswego, Chetopa and Pittsburg. "The Chetopa area obtains its water from the Mississippian formation, which is supposed to have a catchment area in the Ozarks in southwestern Missouri and northwestern Arkansas."

Thirty nine waters from the Ordovician rocks in Missouri varied greatly in fluorine content, as is shown in TABLE VIII (P. 65). Two waters from the Joachim formation contained 5.2 and 6.0 parts per million of fluorine, respectively.

35. Boruff, C. S., and Abbott, G. B. Determination of Fluorides in Illinois Water. Ind. & Eng. Chem., Anal. Ed. Vol. 5, pp. 236-8 (1933).

36. Kehr, R. W. Dental Deficiencies and Drinking Water. J. Am. Water Works Assoc'n. Vol. 23, p. 219 (1931).

These were obtained from wells in Perry County (southeastern Missouri). Another well in Perry County, that of the Frohna Creamery Co., produced water from the Joachim formation, that contained 2.8 parts per million of fluorine. Geologists of the Missouri Geological Survey examined well-drillings from this latter well. They identified "garnet-like" crystals of fluorite in portions of the drillings from the Joachim formation.

The St. Peter Sandstone of the Ordovician Age produced some waters of high fluorine content. Boruff and Abbott[35], report fluorides in the waters of the St. Peter Sandstone of Illinois.

Waters obtained from formations of Cambrian Age in Missouri were relatively low in fluorine content. Thirteen of these contained from 0.1 to 0.7 parts per million of fluorine.

[35] Boruff, C. S. and Abbott, G. B. Determination of Fluorides in Illinois Water. Ind. & Eng. Chem., Anal. Ed. Vol. 5, pp. 236-8 (1933).

TABLE VIII.

Ordovician Formations	Number of Samples	Fluorine Content in P.P.M. Highest	 Lowest	 Average
Plattin	1			0.15
Joachim	4	6.0	1.1	
St. Peter	13	4.2	0.25	2.0
Cotter	7	1.6	0.1	
Jefferson City	6	1.6	0.2	
Roubidoux	8	3.0	0.2	
All Ordovician Age waters	39	6.0	0.1	0.92

(b) Possibility of Mottled Enamel in Missouri

In an investigation of the literature on the subject, no account has been found of the occurrence of this dental defect in the state of Missouri.

Dean[36], in his survey of mottled enamel in the United States, sent questionnaires to eleven "component dental societies" in Missouri. He received only five replies. His reports[36,37], reveal no areas of mottled enamel in this state. According to his map[37], "showing distribution of individual Questionnaires," he surveyed only a limited region in southwestern Missouri, near the Chetopa, Kansas[38] endemic area.

The concentrations of fluorine in Missouri waters, that have been reported in this thesis, would indicate the advisability of a further survey of Missouri for the occurrence of mottled enamel.

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36. Dean, H. T. The Distribution of Mottled Enamel in the United States. op. cit. p. 10 .

37. Dean, H. T. The Distribution of Mottled Enamel in the United States. op. cit. p. 10 .

38. Kehr, R. W. Dental Deficiencies and Drinking Water. op. cit. p. 10 .

Five areas of undetermined boundaries each have been found to contain at least one water supply that possibly may be the cause of mottled enamel. These are tabulated in TABLE IX (p.68).

TABLE IX.

REGION	LOCATION	FLUORINE CONTENT IN P.P.M.
North Central,	Ridgeway, Mo., Harrison County.	2.8
East Central,	Warrenton, Mo., Warren County.	1.4
	Vandalia, Mo., Audrain County.	2.2
Central,	Sweet Springs, Mo., Saline County.	1.2
Southeastern,	Frohna, Mo., Creamery Co., Perry County.	2.8
Southwestern,	Minden Mines School, Barton County.	2.8

REMOVING FLUORINE FROM WATER

Wherever an alternate water-supply may be used, this should be substituted for the one having a dangerously high concentration of fluorine. A number of instances are reported where this course has been followed. Specific examples are: Bauxite, Arkansas, Chetopa, Kansas, and Oakley, Idaho.

Churchill[39], in his pioneer paper on the subject of correlation of mottled enamel with fluorine in the water supply, states: "Two questions are raised by the discovery of unsuspected amounts of fluorine in drinking waters:
First, what physiological effects may be produced by these fluorides?
Second, what can water chemistry contribute to the concentration control of fluorides?"

Considerable progress has been been made in answering the first of these two questions, as is revealed in the extensive literature on the subject of mottled enamel.

With regard to the second of the two questions raised by Churchill, three periodical publications have been found dealing with the subject of fluorine removal from waters.

[39] Churchill, H. V. Occurrence of Fluorides in Some Waters of the United States. op. cit. p. 13.

Some of the methods suggested in the publications mentioned are, as follows:

(a) 40. Dosage with aluminum compounds and subsequent removal of the floc.

(b) 41. Filtration through a river-sand containing two percent, by weight, of powdered aluminum.

(c) 42. Absorption of fluorides by an activated carbon, with the hydrogen-ion concentration of the water maintained at a (pH) value of 3.0, or less.

Several experiments were performed as were suggested by (a)[40], of the above.

(a) Experimental Fluorine Removal by Dosage with Aluminum Sulphate

The following procedure was used:

Four gallons of the Missouri School of Mines tap water, containing 0.1 parts per million of fluorine, were placed in a 5-gallon stone-ware jar.

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40. Boruff, C. S. Removal of Fluorides from Drinking Waters. Ind. & Eng. Chem. Vol. 26, pp. 69-71 (Jan. 1934).

41. Kramer, S. P. The Removal of Fluorides from Water by Sand Filtration. Science. Vol. 80, p. 593 (1934).

42. McKee, R. H. and Johnston, W. W. Removal of Fluorides from Drinking Water. Ind. & Eng. Chem. Vol. 26, pp.849-51 (1934).

A known amount of fluorine, as sodium fluoride, was added to this water.

The calculated amount of lime and sodium carbonate, to give theoretical softening, was added, with the further addition of 170 parts per million of aluminum sulphate. The water was stirred vigorously for thirty minutes, and the floc permitted to sub-side.

After the complete subsidence of the aluminum sulphate floc, the residual fluorine concentration was determined.

The record of several experiments that were performed by this procedure appears in TABLE X (p. 72).

Discussion

The experiments recorded indicated that the dosage of waters with excessive amounts of aluminum sulphate, during softening, may be expected to remove some fluorine, under experimental conditions. This lends corroboration to the published work of Boruff.[43]

Time did not permit any further extension of the experiments here indicated.

[43] Boruff, C. S. Removal of Fluorides from Drinking Waters. op. cit. p. 63 .

TABLE X.

TREATMENT	INITIAL FLUORINE IN P.P.M.	RESIDUAL FLUORINE IN P.P.M.
Softening and Aluminum sulphate.	2.0	1.2
" " " "	2.4	1.5
" " " "	4.4	3.0

(b) Experimental Fluorine Removal By Percolation of Fluorine-bearing Water through Sand and Powdered Aluminum

An attempt was made to remove fluorine from waters by the method of Dr. S. P. Kramer[44].

The water was percolated through a filter bed consisting of a clean, high-silica sand, intermixed with powdered aluminum, as in Experiment I (p. 74). No reduction of the fluorine content of the water was secured.

Personal correspondence with Dr. Kramer revealed that he had used an Ohio River sand, which he stated,* "has a relatively high content of calcium carbonate and of aluminum silicates."

Dr. Kramer supplied sand and aluminum that he had used in his experiments. These were used for Experiments II and III (p.75,77).

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* Letters from Dr. S. P. Kramer, National Institute of Health, U. S. Public Health Sercice, Washington, D. C.

44. Kramer, S. P. The Removal of Fluorides from Water by Sand Filtration. op. cit. p. 70 .

Experiment I.

A sand, obtained locally, was screened to 40-mesh, and was washed free of dirt. To this sand was added two percent of powdered aluminum (Merck)

The sand and aluminum mixture was placed to a height of fifteen centimetres in a glass tube. This tube was 90 centimetres in length and 2½ centimetres inside diameter. A cotton plug, two inches in thickness, served to retain the sand and aluminum bed. The prepared filter tube was held in a vertical position by a clamp attached to a stand. A one-litre tap-funnel was supported above the filter tube.

A solution of fluorine in distilled water was prepared by the addition of 25.0 parts per million of sodium fluoride. This contained 11.3 parts per million of fluorine.

One litre of the fluorine-containing water was permitted to percolate through the prepared filter. The filtrate was collected in 100 millilitre "cuts." These were analyzed for residual fluorine.

The above filtration required 3 hours.

No reduction in the fluorine content of the water was obtained.

Experiment II.

The mixture of sand and aluminum (2% by weight), supplied by Dr. Kramer, was charged into the filter tube of Experiment I, to a depth of 60 centimeters. This change was by the advice of Dr. Kramer*. The sand used was about 20-mesh.

The procedure of Experiment I was used. The filtrates were analyzed for their residual fluorine content with results as appear in TABLE XI (p. 76).

The above filtration required 4 hours.

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* Personal communication.

TABLE XI.

	RESIDUAL FLUORINE IN P.P.M.
Initial Water	11.3
Cuts 1-4 (inclusive)	Yellow in color; not determined.
Cut 5	7.6
" 6	7.4
" 7	7.0
" 8	6.6
" 9	6.0
" 10	5.2

TABLE XII.

	RESIDUAL FLUORINE IN P.P.M.
Initial Water	11.3
Cuts 1-4 (inclusive)	Yellow in color; not determined.
Cut 5	2.6
" 6	2.4
" 7	2.4
" 8	2.3
" 9	2.2
" 10	2.2

Experiment III.

Dr. Kramer supplied a second sample of his sand, which was screened to 40-mesh. In admixture with this sand, he supplied aluminum powder which had been washed with acetone. The washing with acetone served to remove traces of oil from the powder. Its wetting properties were much improved.

This experiment was performed using the above sand, and aluminum in two percent admixture. The procedure was substantially the same as in Experiments I and II.

The filtration required 8½ hours.

Results of this experiment appear in TABLE XII (p.76).

Experiment IV.

This experiment served to repeat Experiment III, with slower filtration through the filter-bed.

Approximately 12 hours were used for the filtration. The extension in time of filtration was secured by maintaining only a very slight head of water above the upper surface of the sand and aluminum bed.

The first four cuts again were yellow in color and their fluorine content was not determined. The remaining 600 millilitres of the filtrate was removed as one cut. The fluorine content of this last cut was found to be 0.5 parts per million.

Discussion

Under certain laboratory conditions, it was found possible to decrease the fluorine content of a water by percolating the water through a filter bed of sand and aluminum. This is a process that has been originated by Dr. S. P. Kramer, of the NATIONAL INSTITUTE OF HEALTH, Washington, D. C. In a personal communication, he informs that he has applied for a patent on his process.

The foregoing experiments (pp. 74-78) appear to indicate that the removal of fluorine from water, by percolation through a sand and aluminum filter bed, may be dependent upon the following factors:

(a) The kind of sand that is used.
(b) The degree of wetting of the powdered aluminum by the percolating waters.
(c) The time of contact of the percolating waters with the sand and aluminum in the filter bed.

Time did not permit an extended investigation of this method for removing fluorine from water.

SUMMARY

1. A brief history of mottled enamel and of its association with fluorine in drinking water has been presented.

2. A brief history of methods for determining fluorine in water has been presented.

3. Tests of the accuracy and of the reproducibility of fluorine analysis by the Sanchis method have been described.

4. A total of 207 Missouri waters have been analyzed by the Sanchis method.

5. The fluorine content of 207 Missouri waters, as analyzed by the Sanchis Method, has been found to range from 0 to 6.0 parts per million.

6. A total of 71 Missouri waters, that were obtained from surface supplies, and from unconsolidated geological formations, have been found to contain from 0.1 to 0.85 parts per million of fluorine. These have been found to have an average fluorine content of 0.31 parts per million.

SUMMARY CONT'D.

7. The fluorine content of 136 waters from rocks of Cambrian, Ordovician, Mississippian and Pennsylvanian Age, in Missouri, has been determined.

8. The possibility of the occurrence of mottled enamel in Missouri has been discussed.

9. An investigation of some methods for removing fluorine from water has been made.

10. A map has been prepared, showing the distribution and fluoride content of certain Missouri waters.

PART B

MANGANESE

INTRODUCTION

Manganese and iron are often found associated in nature. The presence of manganese in waters may be expected whenever iron is present. Corson[45] states, "Waters which contain manganese always contain iron."

Usually, manganese owes its presence in water to the decomposition of organic matter in manganiferous soils. Subsequent leaching of the soil by humic, carbonic, and sulphuric acids, present or formed in percolating waters, dissolves the manganese.[46]

Waters containing iron and manganese are clear and without color when first drawn. They possess no more than a slight content of dissolved oxygen. Exposure to the oxygen of the air precipitates red iron oxide and the darker-colored hydrated manganese oxide. This accounts for the familiar turbidities in some waters.

45. Corson, H. P. Occurrence of Manganese in the Water Supply and in an Incrustation in the Water Mains at Mt. Vernon, Ill. Univ. of Ill. Bul. No. 10, p.57 (1913).

46. Weston, R. S. Manganese in Water, Its Occurrence and Removal. J. Am. Water Works Assoc'n. Vol. 23, p.1272, (1931).

Many reports on the prevalence of manganese in waters have appeared in the literature. Monfort[47] states that manganese is rarely absent from ground and surface waters. Janzig and Montank[48] believe that nearly all waters contain manganese in varying concentrations. Corson[49] states, "manganese is of rather uncommon occurrence in water, although many waters contain at least traces of the element."

The ordinary content of manganese in ground waters is quite low. The New Jersey Department of Health found that 238 of the potable water supplies of that state ranged from 0.03 to 0.20 parts per million in manganese content.[50]

47. Monfort, W. F. Iron and Manganese Troubles. Water Works. Vol. LXV, p. 169 (1926).

48. Janzig, A. C. and Montank, I. A. High Manganese Effluents from Idle Filters. J. Am. Water Works Assoc'n. Vol. 21, p.1319 (1929).

49. Corson, H. P. Occurrence of Manganese in the Water Supply and in an Incrustation in the Water Mains at Mt. Vernon, Ill. op. cit. p. 82 .

50. Weston, R. S. Manganese in Water, Its Occurrence and Removal. op. cit. p. 82 .

Corson examined waters from a variety of sources and found the following distribution of manganese concentrations:

11 streams -- from 0.02 to 9.0 parts per million of manganese,
5 " -- less than 0.02 " " ,
60 wells -- from 0.03 to 2.8 " " ,
87 " -- less than 0.03 " " ,
1 spring -- 7.8 " " ,
3 " -- 0.4 " " ,
6 " -- contained no manganese.

Monfort[51] states that he found 4.5 parts per million of manganese in a water from Excelsior Springs, Mo. This was the highest content of manganese that he found in a Missouri water.

51. Monfort, W. F. Iron and Manganese Troubles. op. cit. p. 83 .

MANGANESE BACTERIA

Many waters contain certain thread-like organisms, commonly associated with iron and manganese. These thread bacteria have the effect of precipitating iron and manganese in the form of their oxides.

Considerable conjecture has been aroused concerning the life process of these organisms. Jessen[52] examined a number of Texas waters for manganese, and for the thread bacteria. He found the two both co-existent, and each present independently of the other. His conclusion was, "manganese is not a food requirement for the organisms which oxidize manganese. The oxidizing of the manganese by these organisms seems rather to be an independent function."

Schorler, as reported by Zapffe[53], found that growth energy is afforded the bacteria when they decompose iron or manganese bicarbonates. The iron or manganese ion is not consumed by the organism, but adheres to its mucilaginous sheathe. There it is oxidized to the corresponding oxide. The role of the organism in depositing the oxides would appear to be that of an "organic" catalyst.

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52. Jessen, F. W. Manganese Bacteria in Waters of Texas. J. Am. Water Works Assoc'n. Vol. 24, p. 87 (1932).

53. Zapffe, C. The History of Manganese in Water Supplies and Methods for Its Removal. J. Am. Water Works Assoc'n. Vol. 25, p. 660 (1933).

The effect of the presence of thread bacteria in public water supplies may be either good or bad. In the first case, their property of precipitating the oxides of iron and manganese may be used in deferrization and in demanganization.[54,55] According to Weston, it is better to depend upon surface contact with accumulations of hydrated oxides and organisms, than upon over-dosing with alkali, for the removal of manganese from waters.

In a filter plant, where no specific efforts are made at iron and manganese removal, thread organisms may deposit the oxides and hydrated oxides of these elements on the filter sand. When the filter is permitted to remain idle for an interval and then put back into use, a high concentration of iron an manganese may appear in the filtered water.[56]

54. Weston, R. S. Manganese in Water, Its Occurrence and Removal. op. cit. p. 82.

55. Zapffe, C. The History of Manganese in Water Supplies and Methods for Its Removal. op. cit. p. 85.

56. Janzig, A. C. and Montank, I. A. High Manganese Effluents from Idle Filters. op. cit. p. 83.

The re-solution of manganese is due to the lack of oxygen in the stagnant water in contact with the filter bed.[57]

Thread bacteria are often responsible for the formation of undesirable incrustations in water mains. This is evidenced by the fact that such incrustations have been found to contain larger proportions of manganese than iron, when Crenothrix is present in the water.* This may occur when the water contains more iron than manganese in solution.

In general, the bad effects of thread bacteria in water outweigh the good. Removal of manganese from water, when necessary, may be secured by more effective methods than by the biochemical one.[58]

* This thread bacteria favors the manganese compounds in water, in preference to those of iron.

57. Boynton, P. and Carpenter, L. V. Manganese and Its Relation to Filters. J. Am. Water Works Assoc'n. Vol.24, p. 1348 (1932).

58. Zapffe, C. The History of Manganese in Water Supplies and Methods for Its Removal. Vol. 25, pp. 673-6 (1933).

METHODS OF ANALYSIS

Numerous methods are available for the determination of manganese. Three methods; the Persulphate[59], the Periodate[60], and the Bismuthate[61], appear to be favored for the determination of this element when it is present in water. Each depends upon the oxidation of manganese to the colored permanganate ion. Colorimetric comparisons are made with standards containing known amounts of manganese. Each of the three reagents, used in the respective methods, act as oxidants. There should be little choice between the methods based upon this property of the reagent.

The presence of chloride ion interferes with the determination of manganese by the above methods. In the Persulphate method, it is removed by precipitation as silver chloride. Taking to "fumes" with sulphuric acid removes chloride in the Bismuthate and Periodate procedures.

59. American Public Health Association. Standard Methods of Water Analysis, Seventh Edition. New York. (1933). p. 51.

60. Ibid. p.52.

61. Association of Official Agricultural Chemists. Methods of Analysis, Third Edition. Washington. (1930) p. 418.

A special distinction between the use of sodium bismuthate and of sodium periodate lies in the fact that an excess of the former reagent is insoluble and must be removed from the sample by filtration. On the contrary, the periodate is soluble and colorless; an excess may be permitted to remain in solution. Periodate standards may be prepared which are stable for months. The inclusion of a suitable excess of the reagent protects the permanganic ion from incidental reduction, and preserves the standard from deterioration. Bismuthate-developed standards, on the other hand, are extremely sensitive to reduction, as they contain no excess of oxidizing reagent in solution. These must be prepared at the time of their use.

Both the Bismuthate and the Periodate method were used for the determination of manganese in Missouri waters. Consistent and comparable results were secured with each. A slight preference was given to the former as more rapid analyses were made in handling a large number of samples when it was used.

Using the Bismuthate method, and a sample of 500 mls. in volue, it was found entirely practicable to determine manganese in waters at a concentration as low as 0.02 parts per million. In addition, the positive presence of manganese below this concentration could be readily discerned. When manganese was present at a concentration below 0.02 parts per million, it was reported as 0.01 parts per million.

The Bismuthate Method

500 mls. of the water sample (proportionally less when the manganese content of the sample was above 0.10 parts per million) were measured into a pyrex beaker. A few drops of concentrated sulphuric acid were added, and the sample was placed on a sand-bath for complete evaporation.

The residue from evaporation was treated with 20 mls. of 1 : 1 sulphuric acid, and heated until evolution of fumes of sulphur trioxide had ceased. The fuming was repeated as often as necessary to drive off all volatile anions, particularly chloride. Except in the case of highly saline waters, two fumings always sufficed. A heating at higher temperatures sometimes proved necessary to eliminate carbonaceous matter from the residue. A Meeker type burner provided the heating necessary for elimination of chloride and carbon.

The fumed residue from the above was taken up in 40 mls. of dilute nitric acid (1 voluem of concentrated nitric acid diluted to 4 volumes). 0.50 grams of sodium bismuthate were added, and the contents of the beaker was stirred to break up the fused sulphates adhering to the bottom. The beaker was placed on a hot-plate, and heated to the appearance of the permanganic ion color.

Heating was continued until the contents of the beaker had evaporated to a volume of ten to fifteen mls.

After removing the beaker from the hot-plate, and cooling to 20° Centigrade, a second 0.50 gram portion of the bismuthate was added. After stirring and permitting to stand for about 5 minutes, the maximum permanganic-ion color had developed. The sample was then filtered through an asbestos mat in a Gooch crucible (which had been previously ignited and washed with a four percent potassium permanganate solution, followed by washing with distilled water). Insoluble bismuthate and other undissolved matter in the beaker was washed on to the filter mat with dilute sulphuric acid (1 volume of concentrated sulphuric acid made up to 40 volumes with distilled water).

Filtrate was transferred to a 50 ml. Nessler tube, and made up to the mark with the 1 : 40 dilute sulphuric acid. Comparison was made immediately with standards prepared as below:

Standards -- Prepared by adding 1, 2, 3, 4, & 5 mls. of a potassium permanganate solution (containing 0.01 mgs. of manganese per millilitre) to a series of 50-ml. Nessler tubes, and diluting to 50 mls. with the 1:40 dilute sulphuric acid.

Whenever the manganese content of a sample exceeded 0.10 parts per million, a second determination was made in which a proportionally smaller volume of water was used for analysis.

The Periodate Method

This method of analysis was used exactly as published in Standard Methods of Water Analysis, American Public Health Association, New York, Seventh Edition, 52, (1933).

DISCUSSION OF MANGANESE IN MISSOURI WATERS

184 Missouri waters have been analyzed for their manganese content. These have been tabulated in TABLE VI (pp. 35-60) of this thesis. Mr. R. T. Rolufs, Chemist of the Missouri Geological Survey has analyzed these waters for their iron content. The results of his analyses appear in tabulation with the manganese determinations.

A map has been prepared (Back Inset of this thesis) which shows the geographical distribution of the waters analyzed for their manganese and iron content. This map distinguishes, by symbolic representation, those waters containing 0.05 or over, parts per million of manganese and those waters containing 0.30, or over, parts per million of iron plus manganese. This scheme of representation is quite arbitrary when applied to all waters, regardless of their use. It has special significance when the domestic water supplies alone are considered. According to the best information available, the sum of these two elements may not exceed 0.30 parts per million without complaints from the users of the water.[62]

62. Janzig, A. C., and Montank, I. A. High Manganese Effluents from Idle Filters. op. cit. p. 83.

Monfort[63] states that the presence of so little as 0.05 parts per million of manganese in waters may cause serious operating difficulties

The manganese contents (highest, lowest, and average) of the waters analyzed in this project are represented in TABLE XII (p. 95), with reference to their surface and geological origins. This tabulation is for convenience of representation, only. The waters analyzed were too few in number and unequally distributed to be truly representative of a particular source classification.

Waters of moderately high manganese content were found in many counties throughout the state of Missouri. Two waters from Jackson County contained 2.0 and 5.6 parts per million of manganese, respectively (pp. 43). The highest manganese content of any city water supply, analyzed in this thesis, was that of Hornersville, Dunklin County. It contained 0.50 parts per million of manganese.

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63. Monfort, W. F. Iron and Manganese Troubles. op. cit. p. 83.

TABLE XII.

A. Surface Supplies and Unconsolidated Formations

		Manganese Content in P.P.M.		
	Number of Waters	Highest	Lowest	Average
Impounded Reservoirs	11	.14	.01	.04
Lakes	6	.09	.02	.045
Rivers and Streams	23	.08	.01	.036
Springs	4	.05	.01	
Alluvial Deposits	6	.50	.03	
Glacial Drift	13	.18	.03	.08

B. Consolidated Formations by Geological Ages

Cambrian	12	.40	.01
Ordovician	37	.28	.01
Mississippian	16	.80	.01
Pennsylvanian	22	5.60	.02

SUMMARY

1. A brief discussion of manganese in water has been presented.

2. 184 Missouri waters have been analyzed for their manganese content.

3. The manganese content of 184 Missouri waters has been found to range from 0.01 to 5.60 parts per million.

4. A map has been prepared showing the distribution and the manganese content of certain Missouri waters.

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