Occurrence of Fluorides in Some Waters of the United States[1]

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Investigators of the dental defect known as mottled enamel seem to agree on two points: the defect occurs in certain geographical areas, and the causal factors seem to be associated with the water supply of those areas. Reference to the complete bibliography on the subject compiled by Kempf and McKay (*2*) shows that no specific common characteristic of the waters from affected areas has been discovered. Following the publication just mentioned, A. W. Petrey of this laboratory spectrographically discovered the presence of fluorides in deep-well water from Bauxite, Arkansas. These deep wells were formerly the source of water used by individuals who show the characteristic dental defect known as mottled enamel. Several months prior to the investigation covered in the report of Kempf and McKay the deep-well supply at Bauxite was abandoned in favor of another supply which has since been found to be free from fluorides.

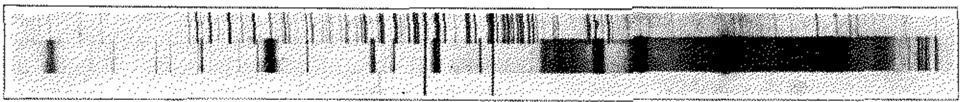

Figure 1—Spectrum of Deep-Well Water

The presence of fluorides was first revealed by means of the spectrograph. Substances containing both calcium and fluoride show a characteristic spectral band which has its head at 5490 Å. and which is degraded towards the infra-red end of the spectrum (*4*). The spectrum obtained from Bauxite deep-well water is shown in Figure 1. The definite and specific character of the 5490 Å. band of calcium fluoride is given in Figure 2 which shows the spectra obtainable from a variety of calcium salts. Only those salts which contain both calcium and fluoride show the characteristic band indicated by the limiting lines in the cases of the spectra of calcium fluoride and that of a mixture of calcium oxide and aluminum fluoride.

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Following the discovery of fluorides in Bauxite deep-well water, the author secured samples of water from other localities where the defect occurs. These localities were Colorado Springs, Col., a well near Kidder, S. D., a well near Lidgerwood, N. D., and Oakley, Idaho. Spectrograms of the water from these localities are shown in Figures 3 and 4. The presence of fluorides is definitely shown in all cases. When the residues from these waters, after evaporation, were tested qualitatively for fluorides by etching methods (*5*) positive tests resulted in all cases. While the etching produced in some cases is slight, nevertheless in all cases it was demonstrably positive.

Quantitative estimation of fluorine is fraught with difficulty. In the author's opinion, determinations for fluorine even with the best available methods tend to give low results. For the determination of fluorine in the samples herein considered recourse was taken to a method of Fairchild (*1*). Since this method was worked out for particular use on phosphate rock, it was necessary to adapt it to the analysis of water. The method, as finally used in the work covered in this paper, follows:

Pipet 100 cc. of water into a 250-cc. glass-stoppered Erlenmeyer flask, add 1 drop of methyl red, and 1.0 *N* hydrochloric acid drop-

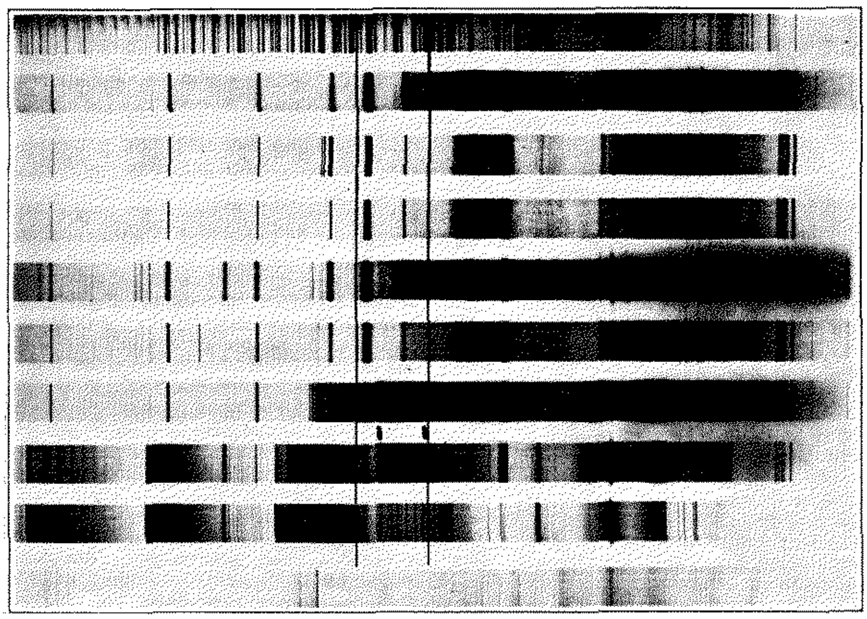

Figure 2—Spectra Obtainable from a Variety of Calcium Salts

Figure 3—Spectrogram of Spring Water

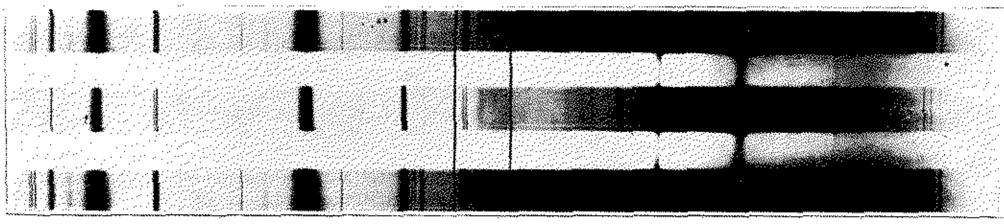

Figure 4—Spectrograms of Various Waters

wise until acid. Add 10 cc. of 20 per cent sodium chloride solution. Filter, wash, and discard any precipitate. Add an excess of 0.08 *M* ferric chloride over that required for completion of the reaction,

$$FeCl_3 + 3NaF = FeF_3 + 3NaCl$$

5 cc. is the proper amount for fluorine content from 0.001 to 0.0100 gram. Add 2 cc. of 1.0 *N* hydrochloric acid and 10 cc. of 5 per cent potassium iodide solution, and stopper the flask. Immerse it in a water bath at a temperature of 38 $\pm$ 1° C. and allow it to remain in the bath 30 minutes. Iodine is liberated by the ferric chloride in excess of that required to react with the fluorine present. Quickly cool the flask, and titrate the iodine with standard thiosulfate solution, using starch as indicator. Simultaneously carry through a control sample with 100 cc. of distilled water and the quantities of reagents used in the analysis. The difference in thiosulfate consumption between the control and the sample represents the ferric chloride consumed in the reaction with fluoride. If the thiosulfate solution contains 4.354 grams of the crystallized salt per liter, it will be equivalent to 0.001 gram fluorine per cubic centimeter.

If the fluorine content shown by the analysis is very low, repeat the analysis, with a larger sample. Evaporate this to 100 cc. in platinum. Do not allow the solution to become strongly concentrated during the evaporation, lest hydrofluoric acid be lost.

Application of this method to various samples from endemic areas yielded the following results:

Location of Sample	Fluorine as Fluoride *P. p. m.*
Deep Well, Bauxite, Ark.	13.7
Colorado Springs, Colo.	2.0
Well near Kidder, S. D.	12.0
Well near Lidgerwood, N. D.	11.0
Oakley, Idaho	6.0

It is well to emphasize the fact that no precise correlation between the fluoride content of these waters and the mottled enamel has been established. All that is shown is the presence of a hitherto unsuspected common constituent of the waters from endemic areas. However, it is of interest to note that apparently the relative severity of the defect in these various areas seems to follow the fluoride concentration.

Since the occurrence of fluorides in potable waters has apparently not been widely studied, a survey of some mu-

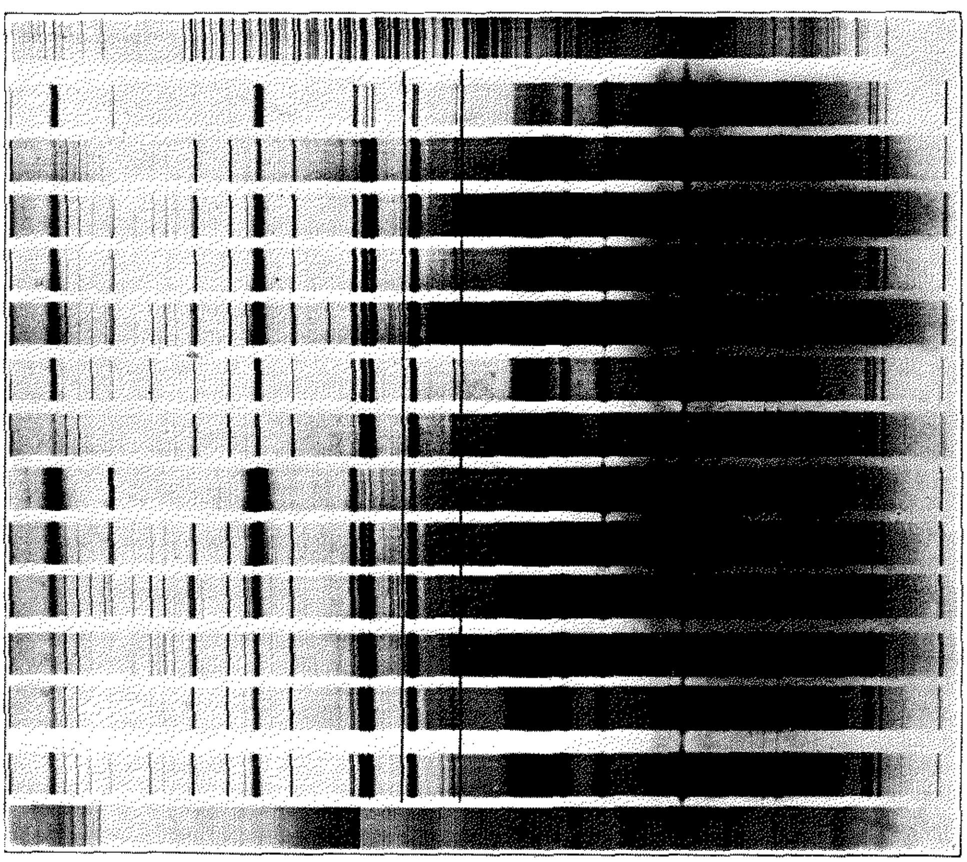

Figure 5—Spectrograms of Various Waters

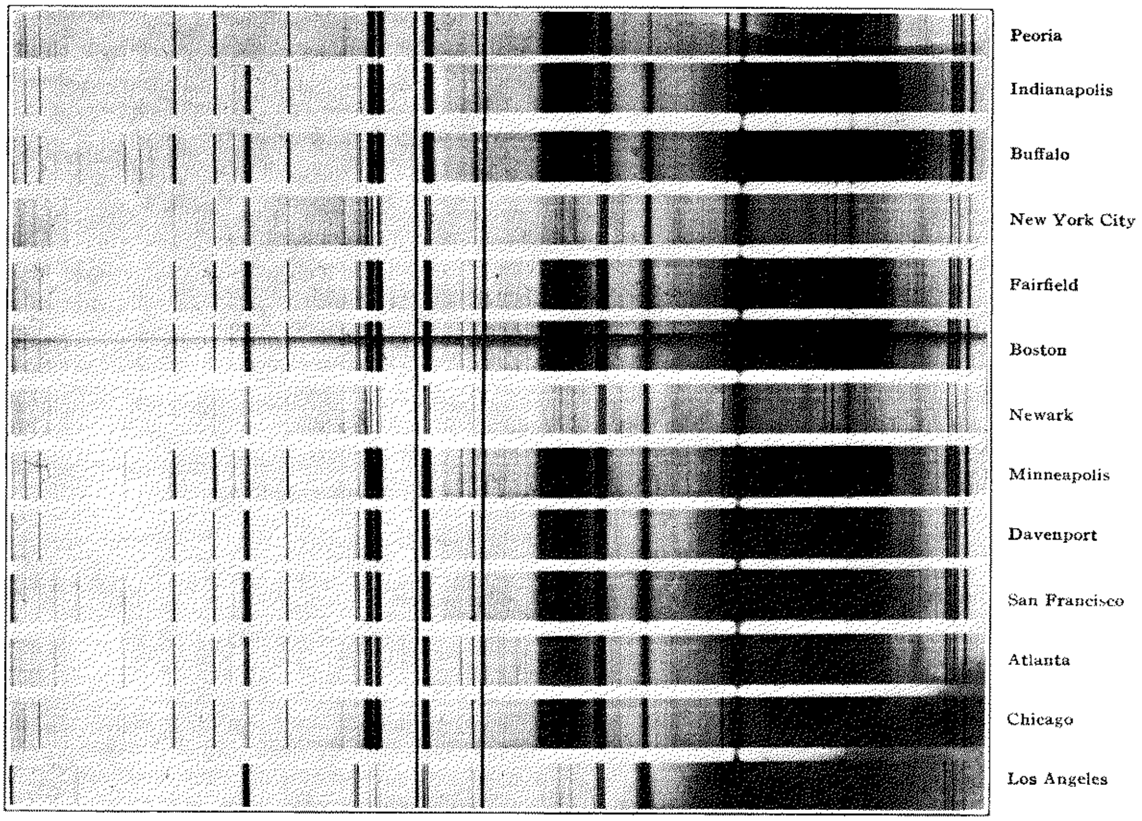

Figure 6—Spectrograms of Various Waters

nicipal supplies in the United States was undertaken with the results as shown in Table I.

Table I—Distribution of Fluorides in Water

Present	Not Present
Cincinnati, Ohio	Philadelphia, Pa.
Milwaukee, Wis.	Washington, D. C.
Birmingham, Ala.	Albany, N. Y.
Pittsburgh, Pa.	Fairfield, Conn.
E. St. Louis, Ill.	New York, N. Y.
Kansas City, Mo.	Boston, Mass.
Toledo, Ohio	Newark, N. J.
Cleveland, Ohio	Chicago, Ill.
Detroit, Mich.	Dallas, Texas
Peoria, Ill.	Atlanta, Ga.
Indianapolis, Ind.	
Buffalo, N. Y.	
Davenport, Iowa	
San Francisco, Calif.	
Minneapolis, Minn.	
Los Angeles, Calif.	

Figures 5 and 6 show spectrograms of the various waters. Quantitative examination of the waters covered in Table I shows the fluorine content in all cases to be less than 1.0 p. p. m.

The geographical distribution of the waters tested is shown in Figure 7, which brings out the interesting fact that traces at least of fluorides are to be expected west of the Appalachians. In no case were fluorides found in waters east of the Appalachians.

Again it is emphasized that no causal connection has been established between the occurrence of fluorides in these waters and the mottled-enamel defect. However, McClure and Mitchell (*3*) report the profound influence of fluorine in the diet upon bone structure. This effect is either the deposition of an apparently abnormal constituent in the bones or the abnormal deposition of a non-calcium constituent as evidenced by an increase in the ash of the bones above normal. They also specifically state that fluorine in the diet at certain levels has a peculiar effect upon the development of teeth. Pending establishment of causal connection between fluorine at certain concentrations in water and the mottled-enamel defect, water chemists might well give attention to the problem of the control of fluoride concentration in drinking water. Two questions are raised by this discovery of unsuspected amounts of fluorine in drinking water: First, what physiological effects may be produced by these fluorides? Second, what can water chemistry contribute to the concentration control of fluorides?

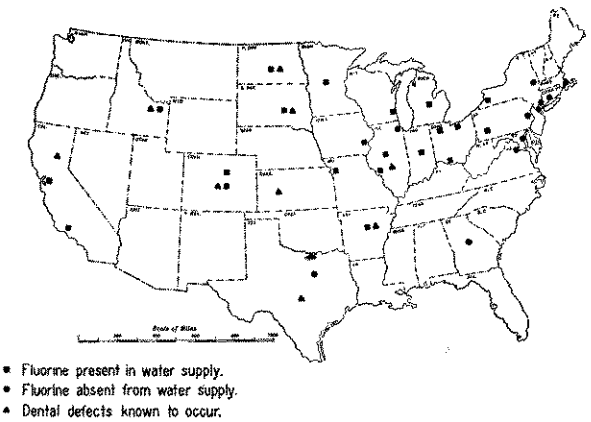

Figure 7—Geographical Distribution of Waters Tested

Acknowledgment

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Literature Cited

(1) Fairchild, *J. Wash. Acad. Sci.*, **20**, 141–6 (1930).
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(5) Scott, "Standard Methods of Chemical Analysis," Vol. I, p. 212, Van Nostrand, 1925.