

FLUORIDE CONTENT OF SOUTH DAKOTA WATER SUPPLIES

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Historical

During the years 1906 and 1907 several dentists of the Rocky Mountain region observed a peculiar condition of the enamel of the permanent teeth which they called "mottled enamel." They knew of no other region where such a condition existed and there was no information concerning the lesion in the literature. Several mottled teeth were sent to Dr. G. V. Black of Colorado Springs for examination. The publishing of the results of his findings in 1916 started work on a problem which has attracted more workers with each passing year.

Many theories have been advanced as to the cause of the lesion known as "mottled enamel" but all were disproved until Dr. O. E. Martin and Dr. F. S. McKay, working in northeastern South Dakota, showed that there was a high correlation between the existence of mottled enamel and the use of artesian water. Chemical analyses of artesian waters were studied and compared with analyses of other waters but no information was obtained regarding the agent causing mottled enamel.

It was not until 1931 that A. W. Petrey of the Aluminum Company of America spectrographically discovered the presence of fluorides in samples of water from Colorado Springs, Colorado; Kidder, South Dakota; Lidgerwood, North Dakota and Oakley, Idaho. Mottled enamel occurred in the regions from which these samples were taken.

Proof that fluorides in the water supply caused the lesion was furnished by M. C. Smith and E. M. Lantz, of the University of Arizona. These workers carried out extensive rat feeding experiments using suspected agents. Only those animals which were given fluorine compounds developed mottled enamel.

The discovery that fluorides in the water supply caused mottled enamel brought out the necessity for an accurate semi-micro quantitative method for determining this ion. None of the methods developed before 1930 were adaptable for the estimation of fluoride ions in the water supply. Since 1930, several colorimetric and volumetric and spectral methods have been developed which will measure micro quantities of fluorides.

Since 1931, surveys as to the fluoride content of water have been made in Arizona, Illinois, Kansas, Rhode Island, Texas, North Dakota, Iowa and Colorado, and wherever the mottled enamel occurred there was always a high correlation between the existence of the lesion and the presence of fluorides in the water supply.

Attempts have been made to remove fluorides from the water supplies by passing the water through filters charged with various types of carbon, iron, aluminum and titanium salts, siliceous absorbents and tri calcium phosphate. Of the materials tested, only one type of carbon, activated aluminum oxide and tri calcium phosphate proved effective in removing fluorides and this ability to remove fluorides was only temporary unless the filter was recharged or regenerated.

Experimental

A. Selection of a Method.

In the selection of a method for routine determination of fluorides in water, several factors were considered and these factors were studied in the light of this problem.

1. The time available must be considered when a large number of determinations are to be made. Accuracy must not be sacrificed for a rapid method, but an accurate rapid method is to be preferred to an equally accurate slower method. An exact colorimetric procedure allowing many simultaneous determinations should be chosen if possible. A number of the methods involving these factors have been developed, but interfering materials frequently occurring in South Dakota waters limit this choice.

2. Materials occurring in the waters examined which could possibly interfere with the fluoride determination are sulphate, chloride, bicarbonate, calcium and magnesium ions as well as organic matter. The sulphate ion, which is present in large amounts in most South Dakota waters, interferes with many colorimetric fluoride determinations; chloride ions also interfere with some of the methods used for analysis; calcium and magnesium ions cause no interference unless present in excess of five hundred parts per million. Since all methods are carried out in an acid solution, the bicarbonates present offer no interfering difficulty. The presence of organic matter causes high results with colorimetric methods using zirconium-alizarin lake but does not interfere in the volumetric method of Willard and Winter¹. Organic matter is not a problem in the analysis of South Dakota waters and the consideration of interfering substances in this study limits itself to the sulphate ions alone and the procedure was chosen with this difficulty in mind.

¹ H. H. Willard and O. B. Winter, *op. cit.* 7.

The most widely used methods for fluoride determination have been:

1. The Fairchild Method²
2. The method of M. D. Foster³
3. The Armstrong modification of the Foster method⁴
4. The volumetric method of Willard and Winter⁵
5. The method of J. M. Sanchis⁶

J. G. Fairchild developed the method for fluoride analysis most widely employed in water surveys before 1932⁷. There are numerous sources of error and the fluoride values obtained by this method are always higher than the values obtained by more recently developed methods⁸. This inaccuracy ruled out its utilization in this investigation.

The procedure of M. D. Foster requires a correction for the sulphate and chloride ions in the water analyzed⁹. It is also necessary to carefully regulate the hydrogen ion concentration of the standards and unknowns, making it a somewhat laborious process to adopt for use in this type of a survey¹⁰.

W. D. Armstrong used acetylacetone in place of the thiocyanate recommended by M. D. Foster¹¹. The advantages obtained by this modification are greater permanency of color and less interference by sulphate and chloride ions. It is a satisfactory method but was discarded for a more rapid procedure.

The method of Willard and Winter, a volumetric procedure, although very accurate, is not applicable due to the excessive time factor¹².

² J. G. Fairchild, *op. cit.* 141.

³ M. D. Foster, *op. cit.* 234.

⁴ W. D. Armstrong, "Colorimetric Determination of Fluorine," *Journal of Industrial and Engineering Chemistry, Analytical Edition*, V (1933), 300.

⁵ H. H. Willard and O. B. Winter, *op. cit.* 7.

⁶ J. M. Sanchis, *op. cit.* 134.

⁷ J. G. Fairchild, *op. cit.* 141.

⁸ M. D. Foster, *op. cit.* 238.

⁹ M. D. Foster, *op. cit.* 234.

¹⁰ W. D. Armstrong, *op. cit.* 300.

¹¹ *Ibid.* 300.

¹² H. H. Willard and O. B. Winter, *op. cit.* 7.

J. M. Sanchis modified the earlier method proposed by Thompson and Taylor, which involved the use of the zirconium-alizarin lake^{13,14}. He sought a rapid method yielding accurate results in the presence of large amounts of sulphate, chloride, bicarbonate anions, and sodium, calcium and magnesium cations. By substituting three normal sulphuric acid for half of the three normal hydrochloric acid used in the Thompson and Taylor method, the fading of the zirconium-alizarin lake due to the sulphate ion was the same in the standards as in the unknowns. This modification eliminated interference up to a concentration of five hundred parts per million of the above ions; also concentration in excess of two hundred parts per million of manganese, fifty parts per million of silicate, up to five parts per million of phosphate, borate, copper or iron ions, as well as any excess of sulphide ions above two parts per million. The method is rapid and many determinations may be made simultaneously. Results agree within 0.2 parts per million, according to J. M. Sanchis. The writers verified these limiting facts in their preliminary investigation.

The Sanchis method can be used for the fluoride determination of many waters, but there is a type of water containing from one to two thousand parts per million of the sulphate ion and this large amount of sulphate ion produces an appreciable fading effect on the zirconium-alizarin lake in excess of that produced by the fluoride and the added sulphuric acid. An attempt was made in this laboratory to lower the sulphate content by precipitation with barium chloride, but this gave low fluoride results.

B. The Elimination of the Interference of the Sulphate Ions

The authors modified the Sanchis method to lower this high sulphate content in the analyzed sample. This was done by using smaller aliquots of the unknowns diluted to one hundred milliliters with distilled water. The range of the standards was changed from 0.0 to 0.30 milligrams of

¹³ J. M. Sanchis, *op. cit.* 134.

¹⁴ T. G. Thompson and H. J. Taylor, "Determination and Occurrence of Fluorides in Sea Water," *Industrial and Engineering Chemistry, Analytical Edition*, VII (1935), 23.

fluoride ion as advocated by Sanchis, to 0.0 to 0.12 milligrams. The color change produced by 0.02 milligrams of fluoride ion in the range of 0.0 to 0.12 milligrams is more pronounced than in the range of 0.12 to 0.30 milligrams, and the upper limit of 0.12 milligrams in the standards is far superior for our purpose to the 0.30 milligram limit suggested by Sanchis.

As a time saving factor, the authors advocate the use of two milliliters of a 1:1 mixture of six normal hydrochloric and six normal sulphuric acids in place of the two milliliters each, added separately, of three normal hydrochloric and three normal sulphuric acids.

As a check on the modifications adopted by the authors, a series of analyses were made for comparison with results obtained by the volumetric method of Willard and Winter¹⁵. Different types of waters were used and concordant results were obtained as noted in Table I below:

Table I

Types of South Dakota Water	Modified Sanchis Method ppm	Willard & Winter Method ppm
Impounded Supply	0.2	0.15
Shallow Well 30 Ft.	0.3	0.3
Hard Artesian	2.0	2.0
Hard Artesian	3.6	3.3
Soft Artesian	6.0	5.8

H. V. Smith has previously checked the Sanchis and Willard and Winter methods so that correlation with equal accuracy has already been established¹⁶.

The Sanchis Method for the Determination of Fluorides, as Modified by the Authors¹⁷

¹⁵ H. H. Willard and O. B. Winter, *op. cit.* 7.

¹⁶ H. V. Smith, "Determination of Fluorine in Drinking Water," *Industrial and Engineering Chemistry, Analytical Edition*, VII (1935), 23.

¹⁷ J. M. Sanchis, *op. cit.* 134.

PREPARATION OF REAGENTS

Standard Sodium Fluoride Solution: Prepare a stock solution containing 2.21 grams of C. P. dry sodium fluoride per liter. Dilute 10 milliliters of stock solution to one liter (1 milliliter equals 0.01 milligram of fluorine).

Indicator: Prepare a stock solution as follows: (a) Dissolve 0.17 gram of alizarin sodium sulphionate in 100 milliliters of distilled water. (b) Dissolve 0.87 gram of crystalline zirconium nitrate, C.P., in 100 milliliters of distilled water.

Add an equal volume of (a) to (b) slowly with constant stirring. Shake at intervals and allow to stand overnight, or until all turbidity has disappeared. Dilute with five volumes of distilled water.

Acid Mixture: Prior to use, mix equal parts of six normal hydrochloric and six normal sulphuric acids.

PREPARATION OF STANDARDS

To each of a series of 250 milliliter Erlenmeyer flasks, add 0, 2, 4, 6, 8, 10 and 12 milliliters of standard fluoride solution (1 milliliter equals 0.01 milligram fluorine) made up to 100 milliliters with distilled water. These standards are treated exactly as the unknowns are treated.

PROCEDURE

A 100 milliliter aliquot of the sample to be analyzed, or a smaller aliquot made up to 100 milliliters with distilled water, freed from turbidity and suspended solids by filtration if necessary, is placed in a 250 milliliter Erlenmeyer flask. To each flask and to the prepared standards add two milliliters of the acid mixture, and then add two milliliters of indicator solution.

Place flasks on a hot plate, bring contents quickly to boiling and remove immediately.

Four hours after cooling, or the following day, transfer the standards to properly labeled 100 milliliter Nessler tubes and make up to the mark with distilled water. Transfer each of the unknowns in turn to a 100 milliliter Nessler tube and compare its color with that of the standards.

Conclusions

Giving due consideration to all data obtained on the waters examined the following conclusions have been reached:

South Dakota water supplies may be divided into the four following groups:

1. Artesian water supplies. These supplies are obtained from deep wells penetrating the Dakota Sandstone and may be divided into two classes, the "soft" and "hard" type. In the same region the hard artesian waters are found at a lower level than the soft artesian waters. Artesian waters may be found in nearly all parts of eastern South Dakota except in a narrow strip along the eastern boundary. Soft artesian wells are most frequently found in Spink, Brown, Day, Marshall, Clark and Kingsbury counties. A few scattered artesian wells are located west of the Missouri River. The fluoride content of the hard artesian waters varies from 2.0 to 3.6 parts per million; the soft type contains from 2.0 to 8.0 parts per million.

Sulphates usually occur in large amounts in both soft and hard artesian water, often in objectionable quantities. Soft artesian waters generally possess a higher bicarbonate alkalinity and a higher chloride concentration than do the hard artesian waters.

Soft artesian waters of South Dakota contain no manganese; hard artesian waters usually contain less than 0.3 parts per million of this element.

In most cases the waters of higher fluoride ion concentration contain more dissolved solids than do the waters of low fluoride ion content.

2. Water supplies from deep drilled wells which have their source just above the Dakota Sandstone. Most of these wells are located in the southern half of the east river section and serve as the source for the municipal supplies for many towns of this region.

The fluoride content of these waters varies from 1.0 to 1.8 parts per million; the sulphate content varies from 550 to 1,000 parts per million; the chloride content is low, and the waters are quite hard.

3. Water supplies from shallow wells and springs. These are found in all parts of South Dakota. The mineral constituents of these waters vary over a wide range; the fluoride content is usually below 1.0 part per million.

4. Water from impounded supplies. These waters usually contain very little dissolved mineral matter, a little organic matter and possess a fluoride content below 1.0 parts per million.

This survey shows a marked correlation between the existence of mottled enamel in South Dakota and the use of waters of high fluoride content, as evidenced by a comparison of the results of this survey with the distribution of mottled enamel in South Dakota as described by H. T. Dean.

Due to the incomplete geologic data on the wells from which samples were taken, it is impossible to fix definitely the sources of the waters studied. It is believed that the section of the State east of the Missouri River draws its water supplies from three artesian flows, from the Niobrara, glacial and river sands. The area west of the Missouri River has more sources from which to draw its water supply. The Foxhills sandstone formation extends across the northern part of this section, with the Lance formation running down into the northwestern corner. In the Black Hills region, the Deadwood and Minnelusa formations serve as sources of water supplies. Across the southern part of this section are the Tertiary, Chadron and White River sands. Artesian flows are available in many parts of the west river region. Shallow supplies are also available.