Importance and Determination of Fluorine in Water

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Introduction

There are certain chemical substances, which if present in drinking water at concentrations greater than definite limits, may be injurious to health. Some of these chemical substances are regarded as essential constituents in drinking water and if they are not present at sufficient concentrations levels, human health is affected adversely.

Fluorine is extensively distributed throughout nature and has been detected in such diverse substances as water, rock and mineral fossils, teeth, foodstuffs and many biological specimens. Interest in the fluorine contents of these materials arises chiefly from the toxic effects of prolonged ingestion of small amounts of fluorine (fluorosis) together with the detrimental results of suboptimum level in the diet.

An average daily diet will provide 0.25-0.35 mg. fluorine. In addition the average adults may ingest 1.0 and 1.5 mg from drinking and cooking water containing 1 ppm of fluorine. Excessive supply (1.5 ppm or more causes mottling of the tooth enamel.

In assessing the safety of a water supply with respect to the above limits of fluorine concentrations, special consideration should be given to the total daily fluoride intake by the individual. If the fluoride concentration in the drinking water of a community is less than 0.5 mg./litre, a high incidence of dental caries is likely to occur. To prévent the dental caries in children a number of communal water supplies are fluoridated to bring the fluorine concentration to 1.0 mg./litre.

Accurate determination of fluorides in water supplies has increased in importance with the growth of the practice of fluoridation of supplies as a public health measure. The maintenance of a constant fluoride concentration is essential in maintaining the effectiveness and safety of the fluoridation procedures. There is, therefore, a need for a method for determination of trace amounts of fluoride which is applicable to wide variety of substances. Ideally the method should also be simple and rapid, as many analyses may have to be carried out on a routine basis. Therefore the purpose of the present article is to discuss the methods which are used for fluorine determination.

Methods of analysis vary with the nature of the starting material and particular interfering material to be removed. Thus urine,[1] the chief medium for the extraction of fluorine from the body, is first evaporated to dryness in the presence of alkali, the residue ashed to destroy organic matter, then the fluoride is distilled to separate it frem interferring ions and finally determined in the distillate. On the other hand, samples of water[2] are frequently analysed directly for fluoride, although more accurate values can be obtained after prior distillation.

Methods for Determination of Fluorine

Titration.[3]—In the titration procedure[4] the thorium nitrate titrant is added to the test solution until a faint permanent pink colour is observed in the presence of the indicator, Alizarin Red S. The same volume of the titrant is then added to a comparison solution which becomes pinker than the test solution.

The final titration is carried out with a standard fluoride solution that bleaches the comparison solution progressively to the matching point.

The titration is carried out in 100 ml Nesseler cylinders. The optical density of the comparison solution, at a wavelength of 520 nm, decreases linearly with volume of the fluoride titrant added. However, the change in optical density is found to be only 0.008 (4 cm. cell) per ml of 10 ppm fluoride titrant, and there is no change in maximum. While a 100 ml Nesseler cylinder has a colour depth of about 30 times that of a 4 cm cell, the human eye is less sensitive than a spectrophotometer, and it is not surprising that many an analyst finds it difficult to obtain consistent results.

2. *Spectrophotometry.—*
   (a) Scot Sanchis Method[5]
   (b) Megregian-Maier Method[5]
   (c) Spands Method[5]
3. Auto Analysis[6]
4. Ion Specific Electrode

Frant and Rose[7] have described a fluoride-sensitive electrode in which the potential developed across a lanthanum fluoride crystal is dependent on the ratio of the fluoride activities on either side of the crystal. As the internal fluoride activity is constant for all practical purposes, the potential developed depends only on the value of the fluoride activity in the external solution. In use, the electrode forms a cell with an external reference electrode, normally the calomel electrode.

Selection of the Method : The distillation procedure is time consuming, potentially hazardous and can only be used by a skilled analyst, as it requires a careful control to obtain reliable results. Recovery of the fluoride depends upon the design of the still, the concentration and nature of the acid used, temperature control and rate of distillation and volume of the distillate collected. Modern techniques are based on the studies and recommendations of Willard and Winter[8] and are satisfactory as the recoveries of fluoride fall regularly in the range of 95-100%. An alternative apparatus, which incorporates a constant temperature jacket of refluxing *syn*-tetrachloroethane, has been described by Samachson, Solvik and Sobel.[9] Some attentionh as been paid to diffusion[10] as an alternative to steam-distillation to effect the fluoride separation. This technique is hardly as less time consuming except, possibly, when many determinations have to be made concurrently.

Most colorimetric methods proposed for the final determination of fluoride depend upon the bleaching action of fluoride ion on a particular organo-metallic dye complex (4, 11, 12, 13 & 14). The fluoride reacts with the dye lake, dissociating a portion of it into a colourless complex anion (ZrF_6^{--}) and the dye. As the amount of fluoride is increased, the colour produced becomes progressively lighter depending on the reagent used. The optimum reaction conditions have been investigated by many workers over the years, but the methods are subject to interference by other ion, which can also form stable complexes with either the metal or the fluoride ion present. A new principle was established in 1959 when Belcher, Leonard and West[15] reported the reaction between the red cerium (III) chelate of alizarin complexone and fluoride ion. The resulting complex is blue, and contains fluorine and cerium alizarin complexone in a 1:1 molar ratio.[16] This is the first positive colour development reaction of the fluoride ion and as a result of these investigations a new colourimetric procedure was evolved.[17] This methods modified by Greenhalgh and Riley[18] has much greater sensitivity than conventional 'bleaching' technique but, unfortunately is still subject to interference from several ions.

Automatic determination of fluoride in sea water and other natural waters are also in use. A technicon Autoanalyzer is used.[19] The method involves the photometric measurement (at 625 nm) of the blue colour formed by F^- with the La chelate of alizarin complexon at pH 4.5. Little or no interference is caused by the major ions present in water, but serious interference is caused by Al^{+++} (720 µg/litre) and by Fe^{+++} and Cu^{++} (7 200 µg per litre).

Thorium nitrate titration is probably the most commonly used titrimetric technique, for the determination of fluoride[20]. Alizarin Red S is widely used as the indicator but the end point is not sharp. By using the methyl thymol blue as the indicator in a solution buffered with glycin perchlorate, the end point has been considerably improved.

A further advance is the recent development of an ion specific electrode [7] for fluoride, which it is claimed, is unaffected by a large excess of common interfering ions and exhibits a Nerstian response over a wide concentration range. This electrode has been used by Raby and Sunderland[21] to determine fluoride in tungsten, following a simple fusion. Fluoride was then determined directly, without the need of any separation step. From this point of view, the electrode appears to be suitable for the determination of fluoride in water and other aquous solutions.

Review of Literature

Previous experience with the titration method had shown that it was subject to considerable personal error because the end-point is rather indistinct, but consistent results can, however, be obtained with it after much practice in observing the end point change. In the original report[22] of the Analytical Methods Sub-committee, great stress was laid on the importance of experimental technique on the accuracy of the results obtained.

The end point for the titrimetric determination of fluoride with thorium nitrate has been improved by the use of methyl thymol blue indicator. Upto 10 mg of fluoride can be determined in a solution buffered with glycin-perchlorate at pH 3.5.

A method for determining fluorine with $CeCl_3$, which forms a stable turbidity, was measured nephilometrically[23] by adding Na_2SO_4, the turbidity increases many times owing to interaction between CeF_3 and SO_4^{--}. To a 2ml sample containing 0.5-14 mg fluorine were added 4 ml each of 0.21 M $CeCl_3$ and Na_2SO_4, and the solution was diluted with water to 100 ml. The absorbance was measured in 2 cm cell. The determination takes 3-5 minutes.

In an improved method [24], known amount of $ZrOCl_2$ and Alizarin Red S (CI Mordant Red 3) are added to a sample of the water and to a 'defluoridated blank' a second sample in which the fluorine (F) has been masked by an Al salt, and the free Al^{+++} have been masked by $Na_2B_4O_7-10\ H_2O$ or HCl). A coloured lake or complex is obtained that undergoes a colour change in the presence of fluoride. The sample and the blank are maintained at approximately the same temperature, and the colour intensities are compared by using a photometer or colorimeter. Special procedures are necessary when the sample initially contains Al^{+++} or PO_4^{---}.

The compound Alizarin Fluorine Blue has achieved considerable use[25] as a reagent for the detection of fluoride and certain metal ions, and as metal chromic indicator. The ideas of Hellmann, PO_4^{---}. and Opitz[26] concerning optimum conditions for amino methylation reaction are applied to the synthesis of Alizarin Fluorine Blue.

A simple rapid method [27] for the spectrophotometric determination of better than 0.1 µg is described. The stability and purity of the reagent have been studied and the optimum conditions for the sensitivity of the reaction established. The method can be applied to the analysis of aquous solutions either directly or, if there are interferences, after a simple micro distillation. Removal of Al^{+++} and SO_4^{--} interference is given in the method.

The need for a simple, reliable test for fluoride in the fluoridation water led to the development of excess Al technique.[28] Two concepts are important in this technique. (i) Fluoride in water can be complexed by adding an excess of Al. The treated water behaves as though it contained no fluoride. (ii) The difference in colour readings between this blank and a second portion of the sample with indicator remains constant thereby allowing the results to be obtained by difference without need to work at any given time and temperature. Alizarin-Zr reagent is the indicator used and gives a colour change from red to yellow with increasing fluoride. The concentration of the interfering substances, other than Al, remains the same in both the blank and sample, and its effect on colour is cancelled out.

A technicon Auto Analyzer is used for automtic determination of fluoride[19]; the method involves the photometric measurement (at 625 nm) of the blue colour formed by F^- with the La chelate of Alizarin complexone at pH 4.5. Little or no interference is caused by the major ion, present in water, but serious interference is caused by Al^{+++} ($>$20 μg/litre) and Fe^{+++} and Cu^{++} ($>$ μg per litre).

An Orion LaF_3 electrode is used [29] and potentials are measured at 25° Vs. a S.C.E. Standarization is carried out with NaF solution and samples are treated with a total ionic-strength adjustment buffer solution (pH 5 to 5.5) containing 1, 2 diaminocyclohexane-NNN'N'-tetracetic acid before potentiometry. Tests on simulated rain water samples by experienced and by inexperienced analysts indicate that the method is suitable for use by unexperienced operators. The method is simple and rapid ($\simeq$20 minutes) and the sensitivity is $\simeq$0.3 μg of soluble F^- per kg.

A cell[30] (with a homoionic liquid junction and commercial halide selective electrodes had been investigated with halide solution of concentration upto 10 molal. The potentiometric response of the appropriate electrode in F, Cl and Br solution is almost theoretical upto concentation of 4 to 5 molar, but in I solution only upto 0.5 molal.

Orion fluoride electrode [31] model 94-09 gives a response to 1-fluoro 2, 4-dinitrobenzene (0.16 to 8 m M) in buffered and unbuffered aqueous solutions although no free F are present. Brief rinsing with water restores the electrode to its original condition. The electrode also responds to Ca^{++} and, after exposure to solution of Ca^{++}, requires a prolonged washing to restore it to its original conditions.

The solution containing F is passed through an anion-exchange resin in the OH form.[32] The adsorbed F are selectively eluted with 0.1 M NaOH, and the elute is passed via a cation-exchange resin in the H^+ form into the calorimeter, in which the HF so obtained reacts with NaOH. The total heat produced is recorded by an integration technique and related to the total amount of F eluted. The method is applicable to 7 μg to 5 mg of F^-.

In gravimetric determination [33] of fluoride by precipitation of bismuth fluoride to 125 ml. of a solution containing 250 mg. of NaF add 1.5 ml. of HNO_3 add 10 ml. of 10% $Bi(NO_3)_3$ solution in 17% acetic acid, followed by 15g. of urea and heat the solution on a water bath for 3.5 hour. After cooling, the precipitate of BiF_3 is filtered off with 10 ml. of 2.5 % acetic acid then with 40 ml. of water. It was washed for 2 hours at 100° and weighed.

A report prepared by the fluorine subcommittee[34] says: 'Many methods have been described for the titration of fluoride ion in aqueous solutions, and several of these methods have been summarised by Mcdonald.[35] These procedures involve the use as titrant of salts of metal cations that combine with fluoride ion to form either insoluble fluoride or stable complex fluoroanions. Titrants that have been used include salts of aluminium, cerium (III), iron (III) lanthanum, thorium, yttrium, zirconium, the most widely used of which for fluoride is undoubtedly thorium nitrate.'

Thorium nitrate was first used by Willard and Winter[8] to titrate fluoride or fluorosilicates in an ethanol water medium, with zirconium Alizarin Red S 'Lake' as indicator. Zirconium was masked by the presence of an excess of fluoride, but at the end point thorium released the zirconium so that it then produced the red colour of its components with Alizarin Red S. However, thorium ion forms a red compound with Alizarin Red S, and Armstrong[36] obtained a sharper end point by omitting zirconium and using the dye alone.

Since then Alizarin Red S has been the most consistently used indicator, but the end point is highly subjective. The colour changes from yellow through various intermediate shades to pink, and operators differ in their preference of the exact hue to record as the end point, it is therefore, necessary for each operator to gain experience of the end point and to make his own standardization of the thorium nitrate solution. In attempts to improve, many dyes have been investigated for secreening effects without much success. The end points obtained with various screening dyes still appear to be subjective, some workers may find screening an advantage, but no single dye has found wide acceptance for this purpose.

Thorium produces coloured compounds with many organic dyes, and these compounds have been examined as possible substitutes for Alizarin Red S; however, none has been widely adopted for use in the titration of milligram amounts of fluoirde. Recently Selig [37] described the use of complexometric indicator, methyl thymol blue, for this purpose.

Different workers have recommended that the titration medium be maintained at pH values ranging from 2.2 to 5.3, but whichever value is selected it is desirable to use a buffer, so that close control of pH can be achieved. The most frequently used buffer is monochloroacetic acid — mono-chloroacetate, for the pH range of 3 to 4. Selig [37] worked out pH 3.35 and used a glycinperchloric acid-odium perchlorate buffer as recommended by Schemidt and Ortloff.[38]

Summary

It is seen that less amount of fluorine intake causes dental caries and greater intake the mottling of teeth. Water suppliers are fluoridated to maintain constant fluoride concentration. Owing to great importance of fluoridation of water supply, it is necessary to know the amount of fluorine present in water.

There are various methods for the determination of fluorine in water, i.e., titration, colourimetric, autcanalysis, ion-specific electrode. Out of these, it is seen that in the titration method the end point is not short. Although the end point has been improved by the use of methyl thymol blue as an indicator, but it is subject to error as it differs from worker to worker.

Most of the colourimetric methods are subject to interferences by various ions present in water, and provision for their removal is pre-requisite. Certain elements have also been found to interfere with auto-analytical procedures.

Ion-specific electrode is considered the best method as it is shown to be less susceptible than the colourimetric method to interferences from other ions in solution, and it gives theoretical recoveries of fluoride added to several drinking water supplies.

REFERENCES

1. Adam, D.F. and Koppe, R.K., *Analyt. Chem.*, 29, 1108 (1957).
2. *The conduct of fluoriation studies in the V.K. and results achieved after five years*, H.M. Stationary Office, London, p. 21 (1962).
3. Crosby, N.T., Dennis, A.L., and Stevens, J. G., *Anal.*, **93**, 643 (1968).
4. *Official Standardized and Recommended Methods of Analysis*, Soc., Analyt. Chem., Cambridge, p. 123 (1963).
5. Ahmad, F., *Standard methods* for *determination of Fluorine*, N.D.V.P Publication (Karachi Centre), p 1 (1974).
6. Grassholf, *Analyt. Abstr.*, **14**, 6486 (1971).
7. Frant, M.S. and Rose, J.W., *Science* Washington, D.C., **154**, 1553 (1966).

8. Willard, H. H., and Winter, O.B. *Ind. Engng. Chem. Analyt. Educ.*, **5**, 7 (1933).
9. Samachson, J., Solvik, N., and Sobel, A.E., *Analyt. Chem.*, **29** 1888 (1957).
10. Hall, R. J., *Analyst*, **88**, 76 (1963).
11. *Standard Methods for Examination of Water and Water Wastes*, Amer. Publ. Health Assoc., N.Y., 12th edn., p. 142 (1965).
12. Cooke, J.R. Dixon; E.J., and Sawyer, R., *Proc. Soc. Water Treat. Exam.*, **14**, 145 (1965).
13. Megregian, S., *Anal. Chem.*, 26, 1161 (1954).
14. *Official Standardized and Recommended Methods of Analysis*, Soc. Anal. Chem., W. Heffer and Sons Ltd., Cambridge, p. 144 (1963).
15. Belcher, R., Leonard, M.A., and West T.S., *Talanta*, **2**, 92 (1959).
16. Leonard, M.A., and West, T.S., *J. Chem. Soc.*, 4477 (1960).
17. Belcher, R., Leonard, M.A., and West, T.S., *Ibid.*, 3577 (1959).
18. Greenhalgh, R. and Riley, J.P., *Anal. Chim. Acta*, **25**, 179 (1961).
19. Chan, K. M. and Riley, J.P., *Anal. Chim Acta*, **35** (3) 365 (1966).
20. Selig, Walter, *Analyst.*, **93**, 118(1968)
21. Raby, B.A. and Sunderland, W.E., *Anal. Chem.* **39**, 1304 (1967).
22. Report of the Analytical Sub-Committee, *Ibid.*, 69, 243 (1944).
23. Bagbanly, I. L. and Alexander, [illegible] A., *Chem. Abstr.*, 74 (8), 94096 (1971).
24. Paulin, A.T., *Anal. Abstr.*, 14, 6478
25. Al-Ani, K., and Leonard, M.A., *Analyst*, 95, 1039 (1970).
26. Hellmann, H. and Opitz, G., *Angew Chem.*, **68**, 265 (1956).
27. Dixon, E.J., *Analyst*, 95, 272 (1970).
28. Paulin, A.T., *Water Engng.*, **71** (859), 371 (1967).
29. Warner, B. Theodore; Bressan and David, J., *Analytic Chim., Acta.*, 63 (1), 165 (1973).
30. Bagg, John; and Rechnitz., G.A., *Analyt. Chem.*, 45 (2) 271 (1973).
31. Zentner and Harry, *Chem. and Ind.*, **10**, 480 (1973).
32. Johanson, Carl, E., *Talanta*, **19** (11) 1349 (1972).
33. Cholakova, J. and L Genov, *Z. Analyt. Chem.*, 261 (2) 127 (1972).
34. Report prepared by Fluorine Sub-Committee, *Analyst*, 97, 734 (1972).
35. Macdonald, A. M.G. Wilson, C.L., and Wilson D.W., ed., *Comprehensive Analytical Chemistry*, Vol. 1, Elsevier Publishing Co., Amsterdam, p. 319 (1962).
36. Armstrong, W.D.J., *Amer. Chem. Soc.*, 55, 1741 (1933).
37. Selig., W., *Analyst.*, 93, 118 (1968).
38. Schmidt, J. and Ortloff, R.Z., *Chemie. Lpz.*, 2, 236 (1965).

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