

## FLUORINE IN DRINKING WATER

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The modern study of the problem of fluorosis (chronic fluorine poisoning) became possible when an Italian, Stefano Chiaie, described, as quoted by Eager (1901), an unsightly dental dystrophy, now known as 'mottled teeth'. The efforts to trace its aetiology have been ceaselessly continued ever since, mainly by American investigators. Outstanding amongst these were Black & McKay (1916), pioneers whose researches led to the discovery made by Smith, Lantz & Smith (1931) that it was the fluorine, contained in drinking water, in a concentration of not less than 1 part per million (1 p.p.m.) and ingested during the period of calcification of the teeth, which was the direct cause of the dental dystrophy. This result was soon followed up by a number of observers, mainly in the United States under the leadership of the dental profession, amongst them physiologists, experimental pathologists, pharmacologists, veterinary surgeons, geologists and analytical chemists. The gate for further research, which in view of its magnitude and importance must be considered as being still in its infancy, has thus been thrown wide open.

In this country Spira (1928) drew the attention of the medical profession to the widespread existence of a symptom-complex which, on clinical grounds alone, he traced to one or more chemical substances contained in aluminium cooking utensils and tap water; and later on (1933) he incriminated, amongst other substances, fluorine in particular as an aetiological factor producing some of the symptoms described. In the same year Ainsworth (1933) found in Maldon, Essex, a number of children afflicted with mottled teeth, and traced the origin of this condition to drinking water containing fluorine in a concentration estimated later by Bowes & Murray (1936) at 5 p.p.m. Wilson (1941) reported the presence of mottled teeth in Cornwall, Somerset, Gloucester, Buckingham, Cumberland and Durham, and Murray & Wilson (1942) found that 28 % of 589 London children between the ages of 10 and 15 had mottled teeth to some extent. In a recent large-scale survey Spira (1942 *a, b*) established the fact that at least 22 % of 5019 men and women examined were afflicted with this condition.

Thus the foundation has been laid for further work in this country on a problem which appears to be of considerable importance from the point of view of public health. Further progress will no doubt help to bring about the elimination of fluorosis, a systemic water-borne disease, of which mottling of the teeth is only one of several external manifestations.

In order to ascertain how a water found on examination by the colorimetric method to contain toxic amounts of fluorine responds to boiling in different cooking utensils (enamel, aluminium, tin, glass, stainless steel) it was allowed by one of us (L.S.) to boil for 5 min. In each vessel the water became turbid, but the degree of turbidity varied in the different vessels. On cooling, the precipitate settled. The supernatant liquid was then examined colorimetrically for fluorine. This experiment was repeated with several samples of water containing fluorine. On each occasion boiling resulted in a considerable reduction of the fluorine content. For example, a sample which contained 1.2 p.p.m. before boiling showed after boiling not more than 0.4 p.p.m., and one which before boiling showed not more than 0.4 p.p.m. became free of fluorine after boiling. It was, therefore, concluded that an amount of fluorine indicated by the difference

between the two estimations had passed into the precipitate. When, however, another portion of the supernatant liquid was examined after the lapse of two or three days its fluorine content was found to have increased, though not to the original level.

This experiment was repeated by the other of us (F.H.G.), who estimated the fluorine content by Sanchis' (1934) method. The samples were drawn on various occasions from a domestic supply which was known to contain appreciable quantities of fluorine. Considerable variations in the fluorine content (between 0.8 p.p.m. and 1.2 p.p.m.) were detected. A sample containing 0.8 p.p.m. of fluorine after boiling for 5 min. and filtration showed 0.2 p.p.m., and the solid residue had appreciable quantities of fluorine in it. This sample of water showed appreciable temporary hardness, and the removal of the dissolved calcium carbonate was apparently responsible for the removal of the greater part of the fluorine. Although there is a possibility that the soluble fluorides combine with calcium carbonate to form an insoluble complex, the removal of the soluble fluorides on boiling is probably mechanical, as a slow re-solution of fluorides takes place if the precipitate is left in contact with water for a time. The 'floc' of calcium carbonate, produced on boiling water containing calcium bicarbonate in solution, probably absorbs the dissolved fluorides, and the slow release of the absorbed fluorides on standing accounts for the gradual increase of fluorides in the supernatant water. The rate at which the fluorides are brought back into solution from the precipitate is shown by the following estimations:

Fluorine content of boiled water	0.2 p.p.m.
Fluorine content of water after standing 2 days in contact with the precipitate	0.5 p.p.m.
Fluorine content of water after standing 7 days in contact with the precipitate	0.7 p.p.m.

The formation of a 'floc' of calcium carbonate by means of the common water softeners such as sodium carbonate and sodium aluminate does not bring about the same degree of removal of fluorine from solution as the formation of a precipitate by boiling, because the fluorine is converted into the extremely soluble sodium salt. The solubility of sodium fluoride is so high that it is hardly likely to be drawn from solution by such a weak absorbent as calcium carbonate. The effect of chemical softeners on the fluorine content of water is shown by the following estimation:

Fluorine content of original water	0.8 p.p.m.
Fluorine content after softening with sodium carbonate	0.8 p.p.m.
Fluorine content after softening with sodium aluminate	0.7 p.p.m.

It was noticed that the physical condition of the precipitate of calcium carbonate differed to a marked extent with the material of the vessel in which the water was boiled. Thus the precipitate produced by boiling in glass or enamelware was very dense and settled rapidly, whilst that produced in aluminium was much lighter and less flocculent. For this reason it was thought possible that the material of the vessel might have some effect on the extent to which fluorine was removed from solution by boiling. Experiments showed, however, that 5 min. boiling in any vessel was sufficient to reduce the fluorine content of the water to a quarter or less of the original. Prolonged boiling had the effect of reducing the fluorine content still further. The results obtained by boiling samples of water in various vessels were as follows:

Fluorine content of original sample of water	0.8 p.p.m.
Fluorine content after boiling for 5 min. in	
(a) Glass	0.2 p.p.m.
(b) Enamelware	0.2 p.p.m.
(c) Tinned iron	0.2 p.p.m.
(d) Clean aluminium	0.2 p.p.m.

The further reduction in fluorine content on prolonged boiling is shown by the following results:

Fluorine content after boiling 10 min. in	
(a) Glass	0.1 p.p.m.
(b) Enamelware	0.1 p.p.m.
(c) Tinned iron	0.1 p.p.m.
(d) Clean aluminium	0.1 p.p.m.

It seems, therefore, that any sample of water containing fluorine above the limit of toxicity and also containing calcium bicarbonate in solution can be rendered innocuous by boiling for 5 min. in any receptacle.

Various methods have been suggested for eliminating the toxic amounts of fluorine contained in the drinking water. The best method is that adopted in some communities in the United States (McKay, 1925,

1933, 1939; Kempf & McKay, 1930; Dean, McKay & Elvove, 1938; Dean & McKay, 1939), namely replacing a water-supply found to produce mottled teeth by one which contains negligible quantities of fluorine. As a result, a new generation, no longer exposed to the danger of ingesting toxic amounts of fluorine, grew up with normal teeth. From the point of view of public health this method would prove the most efficacious one; it would also be the most economical in the long run. It should be kept in mind that the problem of fluorosis is now recognized as not being merely one concerning an unsightly dental appearance alone. Although there is ample evidence to show that dental fluorosis reduces the danger of the teeth becoming carious (Black & McKay, 1916; McKay, 1925; Dean, 1938, 1940; Dean *et al.* 1941; Sognnaes, 1941; Wilson, 1941; Murray & Wilson, 1942), the victims of chronic fluorine poisoning exhibit signs and symptoms of a disease affecting the whole system (Spira, 1928, 1933, 1942c). Amongst these, severe forms of gingivitis similar to, if not identical with, alveolar pyorrhoea appear to be the cause of a considerable proportion of the population becoming edentulous.

Chemical treatment of the water by means of aluminium salts has been employed to reduce the amount of fluorine (Weart & Klassen, 1937; Clawson, Khalifah & Perks, 1940; Greenwood, 1940). Alumina, sodium aluminate and aluminium sulphate have been used as coagulants, and the water allowed to flow into a sedimentation plant. It should, however, be kept in mind that aluminium salts, as shown by Gies (1911, 1916), Steel (1911), Kahn (1911), Schaeffer, Fontès, Le Breton, Oberling & Thivelle (1928, 1929) and Underhill *et al.* (1929), are converted into aluminium chloride under the influence of the hydrochloric acid of the gastric juice; that the aluminium chloride, owing to its astringent and protein precipitating properties, has been found to attack the mucous membrane of the stomach, then to pass in comparatively large amounts from the alimentary tract into the blood circulation and to be deposited in the tissues of the body, thus producing signs and symptoms of chronic aluminium poisoning.

In view of the effect produced on excessive quantities of fluorine present in the drinking water by the chemical treatment with aluminium salts on the one hand and boiling on the other, it is submitted that, being harmless, the boiling method possesses great advantages over the chemical method. The difficulty of preventing the fluorine, which has passed into the precipitate, from going into solution again when allowed to remain in contact with the water for any length of time could be easily overcome, for instance by filtration immediately following boiling.

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