

210 F FLUORIDE

0.1 -2 ppm \ 55 Tests with Blanks

Bleaching of the Zirconium-SPADNS-Complex

- Fill 16mmØ tube with a fully extended syringe (3.2ml) of sample
- Fill a second tube with the same quantity of distilled water
- Add 10 drops of SPADNS-Reagent to each and mix
- Switch on the Photometer 660
- Enter **210** and press **E** for 210 F
- Set filter as indicated to 578nm and press **E**
- Insert tube with distilled water + reagent and press **B**
- Insert tube with sample + reagent and press **M**
- Record as Fluoride ppm (mg/l)

The bonds of the colourless hexafluorozirconate anion (ZrF_6)²⁻ are of considerable strength which give fluorine the potential of requisitioning zirconium from dye complexes with weaker bonds. In these it is typically bound to two neighbouring (*vicinal*) OH-groups. The formerly employed dye Alizarin became progressively replaced after 1958 by SPADNS, 2-(p-Sulfophenylazo)-1,8-dihydroxy-3,6-naphthylene-di-sulfonic acid introduced for this purpose by *Bellack & Schouboe*. SPADNS is the cherry-red product obtained on coupling sulfanilic- with chromotropic acid. The complexation of zirconium with SPADNS results in a bathochromic shift in the direction of violet. Reaction with fluoride reverses this process, to give, contrary to common practice, a reduction of extinction at 578nm. The inherently small reaction contrast is reduced even further by a necessary excess of free SPADNS, to visually appear as nothing more than dark red → cherry red. This excess is necessary to secure complete complexation of all the zirconium with SPADNS. Whereas F : Cl is less than 1 : 100 in water, with rocks the ratio is around 4 : 1. Up to 20% of the fluorine is to be found in Apatite, $Ca_5(PO_4)(F,OH)_2$, the specific mineral phase of phosphorous. This is encountered again as the structural component of teeth, which need to be harder than the regular bone-material based on calcium phosphate. As in the case of rocks, the hardness of dental material depends on the proportional content of fluorine. Since the recognition of this effect in the 1930s there has been an unending debate on the right way of administering sufficient fluoride to the public. Ideal, if hardly ever obtained values for a water supply are considered to range between 1.3 ppm F for cold and 0.7ppm for warm areas.

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