Spectrophotometric Determination of Fluoride
A Comparative Study
and a Suggestion for evaluating Photometric Data

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With 4 figures in the text

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The past thirty years have witnessed a tremendous increase in fluorine chemistry both in knowledge, interest, and industrial applications. Due to its extreme chemical reactivity and consequent poisonous nature on the one hand and its increased industrial use on the other hand, fluorine has become one of the potential industrial hazards. As a result there is a demand for a reliable and quick method for fluoride determination.
McKenna has made a very exhaustive survey of the literature on the existing methods of fluoride determination including gravimetric, titrimetric, colorimetric and conductometric methods. His survey covers the period up to 1950. In view of McKenna's paper no attempt for a detailed discussion of the reported methods will be made here. The aim of the present investigation was to develop a rapid and reliable method for fluoride determination and as such excludes the advisibility of using other methods excepting the colorimetric methods.

All colorimetric methods of fluoride determination depend on the principle decomplexation of a coloured complex through the formation of a colourless fluo-complex, and the amount of fluoride is determined from the extent of bleaching. Such methods have some obvious difficulties. Attempts were therefore first made to use a masked system, so that the masking agent would react with fluoride ion leading to the regeneration of the colour. The amount of colour produced by demasking will depend upon the amount of fluoride. The reaction may be represented by the following scheme:

\[ \begin{align*}
    AB & \quad \text{(Coloured complex)} \\
    + & \quad C \quad \text{(Masking agent)} \\
    \Rightarrow & \quad ABC \quad \text{(Masked system)} \\
    FC \quad + & \quad AB \quad \Rightarrow \quad F' C AB \\
    \text{(Fluo-complex)} \\
\end{align*} \]

Boric acid, phosphoric acid, borates, phosphates were tried to produce masked systems. No positive result was obtained.

The above studies indicated that the only possible approach for the colorimetric determination of fluoride was by measuring the fading of a coloured complex due to the formation of a fluocomplex. There are several such methods reported in the literature. After a detailed study of the literature and some preliminary experimental observation, it was concluded that ferric-tiferronate (1,2-dihydroxybenzene-3,5-disulphonic acid), or ferric-sulfosalicylate or titanium-chromotropic acid systems might give rise to a precise method for fluoride determination. The three systems mentioned above have been thoroughly investigated and their results have been compared with zirconium-alizarin method. Ferric-sulfosalicylate method was found to be the best. The experimental results of only these methods have been summarized and compared.

**Theory**

Due to the presence of more than one equilibrium in the system it is quite likely that Beer's law is not followed by such a system. For comparing such methods where Beer's law is not applicable, one must have a theoretically sound and uniformly applicable way of comparing spectrophotometric data. The usefulness of representing the quantitative