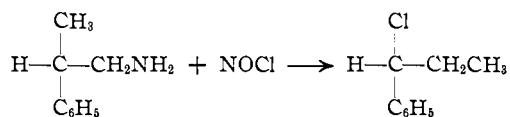


inactive. Similar effects should be expected from the action on the amine of NOCl or NOBr. The active halides should be expected to be the primary. This assumption was made by Levene, Mikeska and Passoth [*J. Biol. Chem.*, **88**, 27 (1930)] and was made the basis of the correlation of the substituted phenylacetic to phenylpropionic acids by Levene and Marker [*ibid.*, **93**, 749 (1931)].

We now find that the active halide obtained by the action of nitrosyl halides on the amine is not a primary but a secondary halide. Thus, in course of the reaction an unexpected rearrangement takes place



inasmuch as this halide leads to $\begin{array}{c} \text{COOH} \\ | \\ \text{H}-\text{C}-\text{C}_2\text{H}_5 \\ | \\ \text{C}_6\text{H}_5 \end{array}$.

A similar rearrangement takes place in the case of 1,1-ethylphenylethylamine (Ref. 2).

It may be mentioned here that the dextrorotatory substituted phenylacetic acids are now correlated to levorotatory substituted 3-phenylpropionic acids on the basis of new evidence. The details will be published in the *Journal of Biological Chemistry*.

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

RECEIVED OCTOBER 21, 1932
PUBLISHED NOVEMBER 5, 1932

P. A. LEVENE
R. E. MARKER
ALEXANDRE ROTHEN

THE COLORIMETRIC DETERMINATION OF FLUORINE IN WATER WITH FERRIC THIOCYANATE

Sir:

In the determination of fluorine in water it has been found most satisfactory to use a colorimetric method based on the fact that the complex ion formed in the reaction between a fluoride and ferric chloride does not give the characteristic iron color with ammonium thiocyanate. Thus, with more iron than is necessary to react with the fluoride, the color is less than that produced by the same amount of iron without fluoride. By determining colorimetrically the quantity of iron reacting with the ammonium thiocyanate, the quantity withdrawn by the fluoride may be found by difference and its equivalent in fluoride read from a curve which has been made by plotting the effect of definite amounts of fluoride upon the amount of iron used in the determination.

The alkalinity of the sample of water must be neutralized and if the volume of the sample is much over 50 cc., it must be evaporated to about

this volume. By using 5 cc. of ferric chloride solution (0.1 g. of iron and 30 cc. of *N* hydrochloric acid in 1 liter) with 10 cc. of ammonium thiocyanate solution (24 g. in 1 liter) in a volume of 75 cc., as little as 0.025 mg. of fluorine in 100 cc. of the sample of water may be determined. If the sample contains more than 0.4 mg. of fluoride, a smaller sample should be taken or more iron used, which necessitates making a new curve for the larger amount of iron. It is important that the acidity, temperature, and volume be more carefully controlled than in the usual thiocyanate determination.

Sulfate produces a similar but very much smaller effect upon the red color but this is also quantitative and a curve showing the effect of definite amounts of sulfate in terms of iron or of fluorine may be made. Then, for each sample, the effect of the sulfate present may be subtracted to obtain the true fluoride content. For example, 200 parts per million of sulfate produced a fading effect equivalent to 0.5 part of fluorine when a 100-cc. sample was used. If the fading of the sample containing this amount of sulfate indicated a fluoride content of 3.7 parts per million, 0.5 part must be subtracted to obtain the true fluoride content of the sample.

Chloride produces a slight fading but for quantities below 500 parts per million this is so small that it may be ignored in a 100-cc. sample. For quantities above 500 parts per million, about 0.1 part per million of fluorine must be subtracted for each 500 parts of chloride present. The chloride added as hydrochloric acid to neutralize the alkalinity must, of course, be taken into consideration. The effect of sulfate and chloride is the same whether they are present as calcium, magnesium, or sodium salts. The amount of nitrate usually found in natural waters has no effect.

This method is particularly adapted to the determination of the small amounts of fluoride to be expected in most natural waters.

U. S. GEOLOGICAL SURVEY
WASHINGTON, D. C.

MARGARET D. FOSTER

RECEIVED OCTOBER 21, 1932
PUBLISHED NOVEMBER 5, 1932