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THE DETECTION OF SMALL AMOUNTS OF FLUORINE IN LARGE AMOUNTS OF CHLORINE

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ABSTRACT

TESTS HAVE BEEN DEVELOPED FOR BOTH THE QUALITATIVE DETECTION AND QUANTITATIVE DETERMINATION OF FLUORINE IN CHLORINE. THE QUALITATIVE TEST IS MADE BY PASSING THE GAS THROUGH MANGANOUS CHLORIDE. IF THE PINK SOLID TURNS BROWN THERE IS GREATER THAN 0.5 PERCENT OF FLUORINE IN THE GAS. THE QUANTITATIVE TEST IS A MODIFICATION OF THE STEIGER AND SHERWIN TEST WITH OXIDIZED TITANIUM SOLUTION.

THE DETECTION OF SMALL AMOUNTS OF FLUORINE IN LARGE AMOUNTS OF CHLORINE

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INTRODUCTION

In a study of the disposal of fluorine it was necessary to know how much fluorine was passing through without reaction. Since in some of the tests 100% fluorine was being passed through the reactor, this necessitated a test which would detect small amounts of fluorine in almost pure chlorine.

Due to the oxidizing action of chlorine, the bleaching action of fluoride ion on various alizarin lakes was of no value. An attempt was made to use the etching action of hydrofluoric acid to break fine glass filaments; this test was partly successful, but the manipulation required was too delicate. The color change of various inorganic chlorides on reaction with fluorine was tested and manganous chloride tetrahydrate was found to turn from light rose to dark brown when a concentration of fluorine greater than 0.5 percent was passed over it. Chlorine does not effect the color of this salt. This test was satisfactory

for a qualitative test, but was of no value as a quantitative test.

It was found that the test of Steiger (1) and Merwin (2) could be adapted to give a reliable quantitative determination. In this test, titanium is oxidized with hydrogen peroxide to give a brown color, and the bleaching of the color is a test for fluoride ion. If a large excess of hydrogen peroxide is used, the chlorine will react with the peroxide and will not bleach the oxidized titanium compound. A large excess of peroxide has no effect on the bleaching action of the fluoride. To make the method quantitative, it must be calibrated with various known gas mixtures.

The quantitative method is accurate to about 10% of the value of fluorine reported if the calibration has been done carefully. Between 0 and 5% of fluorine in chlorine can be determined in this manner.

There are no common gases which interfere with the qualitative test. Obviously any volatile fluoride will interfere with the quantitative test. Hydrofluoric acid will be the usual source of interference in commercial fluorine.

The following experimental procedure is for the quantitative method:

APPARATUS

1. Photoelectric Colorimeter.

   The Fisher Electrophotometer or any other similar photoelectric colorimeter may be used.

REAGENTS

1. Titanium Sulfate

   Dissolve 2.5 g. of $TiOSO_4$ or an equivalent amount of any other titanium salt in one liter of 1:6 sulfuric acid. If the solution is not clear, filter.

2. 12 N Sulfuric acid.

3. 30% Hydrogen Peroxide.

PROCEDURE

Mix 10 ml. of the titanium sulfate, 3 ml. of the hydrogen peroxide and 5 ml. of 12 N Sulfuric acid. Dilute the solution to 100 ml. and mix thoroughly. Fill a tube 25 cm. X 2 cm. three quarters full of this solution and save the remainder for a standard. (Any type of standard gas absorption bottle may be used for this purpose.) Pass the gas through the solution for one minute at a rate of 50 ml. per minute. Remove the solution from the absorption cell and put a small amount in the colorimeter cup (25 ml. cell.) Pour the solution back and forth into the cup several times to remove dissolved gas. Set the transmission of the untreated solution at 86% and compare the transmission of the treated solution with it, using the green filter. (Transmission maxima at 520 millimicrons.) The amount of fluorine which has passed into the solution may be determined by consulting a curve similar to Figure 1.

PREPARATION OF STANDARD CALIBRATION CURVE

Make a series of mixtures of fluorine in chlorine (or nitrogen) containing between 0.5 and 5 percent of fluorine by the partial pressure method. Pass these gasses through the solution as outlined above and measure their transmission setting the unreacted solution at a setting of 86%.

DISCUSSION

With 3 ml. of hydrogen peroxide added to the solution pure chlorine can be passed through the solution for about 7 minutes without

causing any bleaching.

Rather than pick an arbitrary figure for the setting of the standard, the solutions may be read in the colorimeter by setting the unknown at 100 percent transmission and comparing the transmission of the standard to it.

REFERENCES

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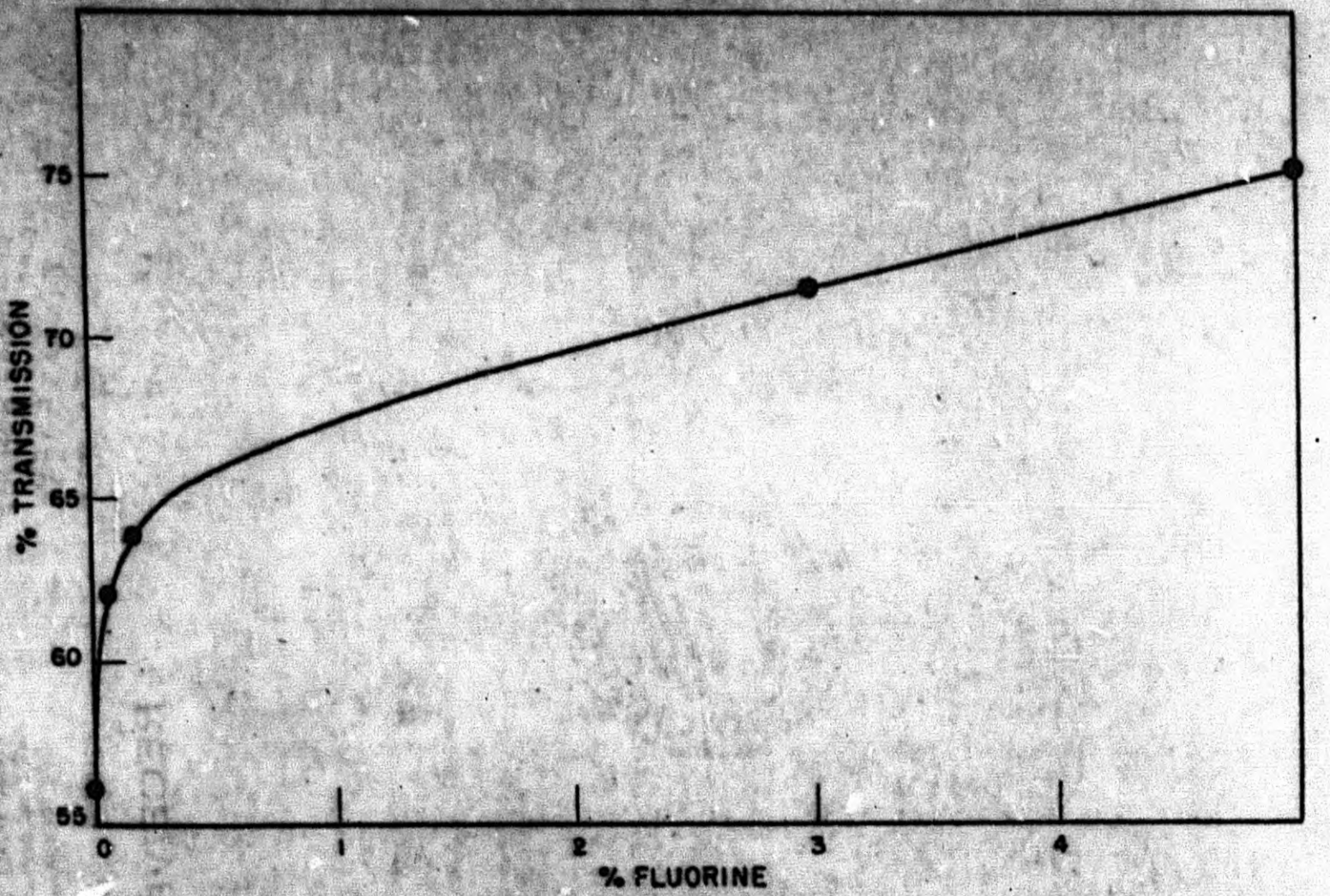
% TRANSMISSION
75
70
65
60
55
0
1
2
3
4
% FLUORINE