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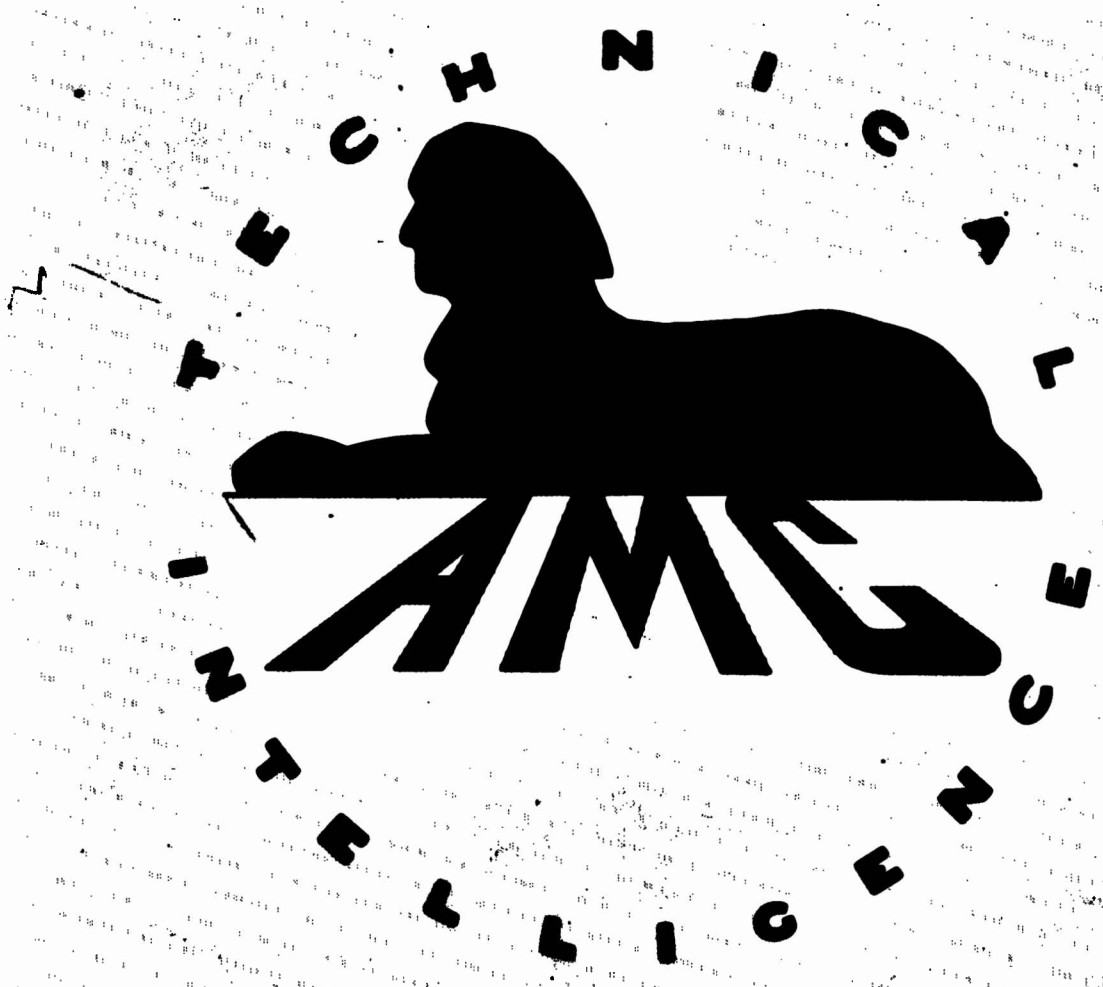

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Division 9
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

# COLORIMETRIC DETERMINATION OF FLUORINE IN FLUORO-ORGANIC COMPOUNDS

to
March 6, 1944
by
John H. Yoe, Official Investigator,
and Lyle G. Overholser

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# COLORIMETRIC DETERMINATION OF FLUORINE IN FLUORO-ORGANIC COMPOUNDS

Service Directive: CWS-P 6

Endorsement (1) From Dr. Carl Niemann, Division Member in Charge to Dr. Walter R. Kirner, Chief, Division 9.

Forwarding report and noting:

> "The fluorine content of organic fluorine compounds can be determined by refluxing the sample, in solution in hexanol-1, with sodium, extracting the liberated fluoride ion with water and estimating the fluoride ion in the aqueous extract by a colorimetric procedure based on the bleaching of a thorium-alizarin lake. The method is applicable to those cases where a hexanol solution of the sample can be prepared."

(2) From Dr. W. R. Kirner, Chief, Division 9 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and concurring.

This is a progress report under Contract 9-344, OEMsr-139 with the Rector and Visitors of the University of Virginia.

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# CONTENTS

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# Colorimetric Determination of Fluorine in Fluoro-Organic Compounds

By
John H. Yoe (Official Investigator)
and Lyle G. Overholser

University of Virginia

## A B S T R A C T

A thorium-alizarin lake was recently (1945) used by Talvitie for the colorimetric determination of fluoride in natural waters. We have applied this method to the determination of fluorine in fluoro-organic compounds after the latter have been refluxed with sodium in 1-hexanol (or other high boiling alcohol) to convert the fluorine into sodium fluoride.

The method will detect 0.1 p.p.m. of fluoride but for most accurate results the concentration should be about 1 p.p.m. At this concentration the accuracy is ±5% when color comparisons are made in 50 ml. Nessler tubes (220 mm.). Values for fluorine were in good agreement with those obtained by the volumetric method in which the fluoride ions are titrated with thorium alizarin sulfonate as indicator. (See Yoe, Salsbury and Cole, N.D.R.C. report dated February 29, 1944).

The thorium-alizarin colorimetric method for fluoride may be used as an alternative procedure in the analysis of fluoro-organic compounds.

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## Colorimetric Determination of Fluorine in Fluoro-Organic Compounds

The colorimetric methods considered for the determination of fluorine involve either the bleaching of a colored solution or repression of the color development by fluoride. In the presence of fluoride, the reaction between ferric iron and iodide is inhibited but the results observed indicate that the reaction is not satisfactory for a colorimetric method. Fluoride bleaches the green colored complex formed by ferric iron and 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Ferron); under optimum conditions it is possible to detect 1 p.p.m. of fluoride by this reaction. Colorimetric methods have been reported for determining fluoride by the bleaching effect on the zirconium-alizarin lake but the reaction has some disadvantages. Recently, N. A. Talvitie [Ind.Eng.Chem., Anal.Ed., 15, 620 (1943)] has used thorium nitrate and alizarin for the colorimetric determination of fluoride in natural waters. We have applied this method to the determination of fluorine in fluoro-organic compounds after the latter have been refluxed with sodium in 1-hexanol (or other high boiling alcohol).

Reagents. 1. Standard Fluoride Solution. Dissolve either 0.0221 g. of sodium fluoride, NaF, or 0.0495 g. of potassium fluoride, $KF.2H_2O$, in water and dilute to a liter. Solution contains 0.01 mg. of fluoride per ml. If desired, the solution may be standardized by the PbClF method.

2. Thorium Nitrate Reagent. Dissolve 0.240 g. of thorium nitrate, $Th(NO_3)_4.4H_2O$ and 61.8 g. of sodium sulfate, $Na_2SO_4$, in water. Add 39 ml. of formic acid (sp. gr. 1.2, 85%) to the mixture, 17.4 g. of sodium hydroxide and dilute to 500 ml. Solution is 0.00087 M with respect to thorium nitrate and 0.87 M with respect to each of the following: Sodium sulfate, sodium formate and formic acid.

5. Sodium Alizarin Sulfonate. Aqueous solution containing 0.0744 g. of sodium alizarin sulfonate per liter.

4. Nitric Acid. Dilute c.p. concentrated nitric acid to approximately 0.5 N.

Preparation of Standard Series. The series may be prepared for the range 0 - 0.12 mg. of fluoride at 0.01 mg. intervals. Transfer the required volume of fluoride solution to a 100 ml. volumetric flask, add 5.0 ml. of alizarin solution and dilute to approximately 90 ml. with water. Add 5.0 ml. of the thorium solution, make up to the mark and mix thoroughly. Transfer to 50 ml. Nessler tubes (220 mm.).

Procedure. Place a weighed sample (Ca. 7-24 mg.) together with 0.2 g. of sodium chips in a 50 ml. g.s. flask provided with a reflux condenser. Add 15 ml. of 1-hexanol (b.p. 155-156°C.) through the condenser and reflux the mixture gently for ten minutes. Extract the hot solution with two 10 ml. portions of water. Dilute the aqueous extract (lower layer) to 50 ml. of water. Transfer an aliquot of this solution to a 100 ml. volumetric flask, add 5.0 ml. of sodium alizarin sulfonate and adjust the acidity by adding 0.5 N nitric acid until the solution is yellow. Dilute to approximately 90 ml., add 5.0 ml. of the thorium solution and proceed as with the standards. The solution may be matched after 30 minutes. Results are calculated directly from the fluoride content of the standard matching the unknown.

Isoamyl alcohol, 1-octanol and 2-methylcyclohexanol were also used as reflux media. Results are given in the following table, together with fluorine values obtained by the volumetric method described by Yoe, Salsbury and Cole in N.D.R.C. report dated February 29, 1944.

| Compound Analysed | Reflux Medium | Mgs. of Fluorine Taken | Mgs. of Fluorine Found Colorimetric Method | Volumetric Method |
|---|---|---|---|---|
| Sodium fluoro-acetate | 2-methylcyclo-hexanol | 2.26 | 5.00 | 2.98 |
| " " | isoamyl alcohol | 2.19 | 2.18 | 2.07 |
| " " | " " | 1.70 | 1.41 | 1.39 |
| " " | " " | 4.00 | 3.85 | 3.87 |
| " " | " " | 4.27 | 3.40 | 3.52 |
| " " | " " | 2.40 | 2.31 | 2.41 |
| " " | " " | 2.49 | 2.49 | 2.53 |
| " " | " " | 2.15 | 2.02 | 2.08 |
| " " | " " | 1.72 | 1.71 | 1.65 |
| Methyl fluoro-acetate | " " | 2.53 | 2.38 | 2.34 |
| " " | 1-hexanol | 2.59 | 2.48 | 2.44 |
| Di-isopropylfluoro-phosphate | " | 2.07 | 1.86 | 2.04 |
| β-Fluoroethanol | " | 2.66 | 2.41 | 2.36 |
| " | 1-octanol | 2.66 | 2.36 | 2.34 |
| Potassium fluoride | water | 1.86 | 1.87 | 1.93 |
| " " | 1-hexanol | 2.87 | 2.81 | 2.87 |
| " " | " | 2.28 | 2.48 | 2.40 |

Note.- Isobutyl alcohol interferes in the colorimetric method.

Remarks. New standards should be prepared each day since the tint changes slightly on aging. If the approximate fluoride content is known, only four or five standards covering the desired range need be prepared. The standards may also be prepared in 50 ml. volumetric flasks, if desired, by using half of the amounts of the reagents given in the procedure.

The method will detect 0.1 p.p.m. of fluoride but for most accurate results the concentration should be around 1 p.p.m., i.e., 0.1 mg. of fluoride in a volume of 100 ml. or 0.05 mg. if the standards and unknowns are made up to only 50 ml. In using aliquots, the sample size shouuld be chosen so that the concentration lies within the optimum range. The accuracy obtainable is ±5% at fluoride concentration of 1 p.p.m. Results obtained by the colorimetric method agreed with those obtained by titration of the fluoride samples with thorium nitrate using sodium alizarin sulfonate as indicator.

The adjustment of the acidity with nitric acid should be done carefully

because the pH must be controlled closely in order to obtain consistent results. Large amounts of sodium nitrate cause low results. However, 100 mg. of sodium nitrate may be present without significant error.

## SUMMARY

A thorium-alizarin colorimetric method for fluoride is presented as an alternative procedure in the analysis of fluoro-organic compounds. It will detect 0.1 p.p.m. of fluoride but for most accurate results the concentration should be about 1 p.p.m. At this concentration the accuracy is ±5% when matchings are made in 50 ml. Nessler cylinders (220 mm.).

Values for fluorine by the colorimetric method are in good agreement with those obtained by the volumetric method described by Yoe, Salsbury and Cole in N.D.R.C. report dated February 29, 1944.

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ABSTRACT:

The fluorine content of organic fluorine compounds can be determined by refluxing the sample, in solution in hexanol-1, with sodium, extracting the liberated fluoride ion with water and estimating the fluoride ion in the aqueous extract by a colorimetric procedure based on the bleaching of a thorium-alizarin lake. The method will detect 0.1 p.p.m. of fluoride but for most accurate results, the concentration should be about 1 p.p.m. At this concentration the accuracy is ±5% when color comparisons are made in 50 ml Nessler tubes (220 mm). Values for fluorine were in agreement with those obtained by the volumetric method in which the fluoride ions are titrated with thorium alizarin sulfonate as indicator.


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