DP-1004

AEC RESEARCH AND DEVELOPMENT REPORT

DETERMINATION OF FLUORIDE BY PYROHYDROLYSIS AND AUTOMATED COLORIMETRY

D. E. HARRINGTON and R. S. DORSETT

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DETERMINATION OF FLUORIDE BY PYROHYDROLYSIS AND AUTOMATED COLORIMETRY

by

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Approved by

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CONTRACT AT(07-2)-1 WITH THE
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ABSTRACT

A pyrohydrolytic-colorimetric method was developed for the determination of fluoride in the presence of high concentrations of interfering elements. Adaption of the colorimetric reaction of fluoride with the lanthanum chelate of alizarin complexone to an automated system gave a minimum detectable limit of 0.050 μg/ml of fluoride in pure solutions and 25 μg of total fluoride in samples that required the pyrohydrolytic separation from interferences. The relative standard deviation of the method is better than 1% at twenty times the limit of detection.

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DETERMINATION OF FLUORIDE BY PYROHYDROLYSIS AND AUTOMATED COLORIMETRY

INTRODUCTION

In studies associated with the development of new reactor fuels and with the development of chemical separation processes, fluoride analyses are frequently required at the Savannah River Laboratory. For example, the fluoride content of uranium dioxide is of interest from the standpoint of possible reactions with the aluminum and Zircaloy cladding of reactor fuels. Also, the concentration of fluoride in acid solutions is important in the dissolution and subsequent processing of thoria and other fuels. Therefore, a routine analytical method was needed for determining trace as well as macro quantities of fluoride in a variety of solid and liquid samples.

Difficulties were encountered in applying the Willard-Winter distillation(1) followed by an indirect colorimetric analysis(2) to the determination of trace quantities of fluoride in solid uranium dioxide and in solutions containing both high nitrate concentrations (>1M) and complexing agents, such as zirconium, aluminum, and thorium. With samples containing less than 200 μg of fluoride, recoveries from the Willard-Winter distillation were generally low and erratic. Further, nitrates and sulfates that were distilled with fluoride interfered with the indirect colorimetric analysis. A microvolumetric method(3) utilizing thorium nitrate as a titrant and Alizarin Red S as the indicator did not give reproducible results with samples containing only micrograms of fluoride, required comparison standards for satisfactory end point detection, and was subject to interference from sulfate.

A direct colorimetric method(4,5) for fluoride that was insensitive to relatively high concentrations of chloride, nitrate, and sulfate was reported by Belcher and associates. The method was based upon the blue complex formed when fluoride reacts with a cerous chelate of alizarin complexone (3-aminomethylalizarin-NN-diacetic acid). The blue complex contains fluoride and the chelate in a 1:1 mole ratio(6) and was used in measuring fluoride in deposit gauge samples(7) and in sea water.(8)

An alternative to the Willard-Winter distillation was a pyrohydrolysis procedure(9) developed by Warf and associates. Pyrohydrolysis, the reaction of a substance with steam at elevated temperatures, liberates fluoride as hydrogen fluoride from a variety of solid materials, including aluminum, zirconium, and gelatinous silica, because of favorable equilibrium constants and high reaction rates at elevated temperatures. The general reaction is:

$$M(F)_x + xH_2O \xrightarrow{\Delta} M(OH)_x + xHF\uparrow \qquad (1)$$

Warf classified fluorides into two fairly distinct groups—a rapidly hydrolyzable group and a slowly hydrolyzable group. The first group included fluorides of aluminum, thorium, uranium, zirconium, and rare earths. The second group included fluorides of the alkali metals, the alkaline earth metals, and beryllium. Sodium fluoride is one of the most difficult fluorides to hydrolyze. However, Warf reported that any slowly hydrolyzable fluoride when mixed with U_3O_8 could be completely hydrolyzed in less than 30 minutes. The over-all reaction was presumed to be:

$$6NaF + 2U_3O_8 + 3H_2O + O_2 \xrightarrow{\Delta} 6HF + 3Na_2U_2O_7 \qquad (2)$$

Warf's pyrohydrolysis procedure was applied only to solid samples and was limited in its sensitivity by a volumetric titration of the liberated hydrogen fluoride.

Powell and Menis(10) used a pyrohydrolysis technique with oxygen saturated with water vapor as a sweep gas to provide a more rapid analysis and also to improve sensitivity by yielding a final volume of condensate that was relatively small. A procedure was given for the analysis of liquid samples as well as solid samples. Liquid samples were made alkaline, evaporated to dryness, and then treated with an accelerator before pyrohydrolysis. Fluoride in final condensates was measured by acidimetric titration. In the presence of chloride, nitrate, or small amounts of sulfate, fluoride was determined by spectrophotometric titration with thorium nitrate using Alizarin Red S or thoron as the indicator.(11) Although directions were given for the analysis of liquid samples, Powell and Menis reported data showing the effect of variables on fluoride recovery from solid samples only. Also, their choice of methods for final measurements of fluoride was dependent on the sample composition.

Because of deficiencies in the reported methods that prevented their application to the types of samples encountered at the Savannah River Laboratory, a study was undertaken to develop a reliable separation-determination sequence. The pyrohydrolysis methods of Warf, Powell, and Menis and the direct colorimetric method of Belcher were selected as most promising for modification into a general method.

SUMMARY

A general method was developed for determining trace as well as macro quantities of fluoride in solid and liquid samples. In relatively pure fluoride solutions, 0.050 μg/ml was detectable by an automated colorimetric method based on the blue complex formed between fluoride and the lanthanum chelate of alizarin complexone. A precision of 0.6% ($P = 0.95$, $n = 6$) was obtained at the 0.3 μg/ml level with standard sodium fluoride solutions.

With samples containing uranium, aluminum, zirconium, and other interfering cations, fluoride is separated by pyrohydrolysis with superheated steam enriched with oxygen and is absorbed in a solution of sodium hydroxide. Fluoride in the solution is then measured by the automated colorimetric method. Under these conditions, 25 μg of fluoride in the original sample was detectable, and a precision of 1% ($P = 0.95$, $n = 4$) was obtained in the analysis of aliquots of standard sodium fluoride solution containing 475 μg of fluoride. The combined pyrohydrolysis-colorimetric method was applied successfully to a variety of solid and liquid samples, including samples of uranium dioxide.

DISCUSSION

The development of a general method for determining trace as well as macro quantities of fluoride in solid and liquid samples containing uranium, aluminum, zirconium, sulfate, and other interfering cations and anions involved:

- Adapting a precise automated method for measuring fluoride in absorbent solutions from pyrohydrolysis.
- Finding the proper conditions for the quantitative separation of fluoride from solid and liquid samples by pyrohydrolysis.

COLORIMETRIC DETERMINATION OF FLUORIDE

A direct colorimetric method for fluoride[4,5] was investigated for application at the Savannah River Laboratory. Lanthanum was used in place of cerium to form a chelate with alizarin complexone because of the resulting increased sensitivity in the final fluoride determination. The method was also automated to further increase the sensitivity, to increase the precision, and to decrease the time required per analysis. The "AutoAnalyzer,"* an automatic colorimeter, was used for the analysis.

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* Product of Technicon Controls, Inc., Chauncey, New York.

The operating principle of the "AutoAnalyzer" involves the continuous injection of a sample into a flowing reagent stream and has been described.(12) The "AutoAnalyzer" consists of several modules and auxiliary equipment. The assembly used in this work included a colorimeter with 10-mm flow cell, a recorder equipped with a range expander, a two-speed proportioning pump, and glass mixing coils. In the automated method, fluoride reacts with a purple chelate of lanthanum and alizarin complexone to produce a blue complex at a pH of 4.5. The absorbance of this complex is measured at 625 mμ. A 30-minute delay time required for development of color in the manual method is unnecessary in the automated method because in the "AutoAnalyzer" color development proceeds to a constant fraction of completion. The average time required per analysis is 7 minutes.

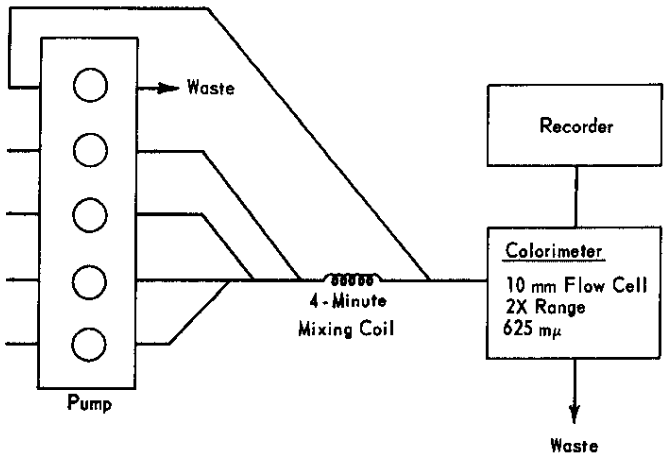
The automated method is applicable to the direct determination of fluoride in aqueous samples where no interferences are present and in the condensate from pyrohydrolysis separations. The flow diagrams for two manifolds used to cover the range 0.050 to 10 μg/ml are shown in Figures 1 and 2. Linear calibration curves are obtained for the ranges indicated by each manifold. The precision of the automated method is summarized in Table I. Interferences in the method are summarized in Table II. Reagents used are described in the Appendix.

TABLE I

Precision of the Automated Fluoride Method

	Concentration, μg/ml	Precision, %	
0.050-1 μg/ml Manifold (Figure 1)	0.050	11.1	(P=0.95, n=6)
	0.100	10.0	
	0.200	6.4	
	0.300	0.6	
	0.400	0.4	
	0.500	0.3	
	0.600	0.2	
	0.700	0.5	
	0.800	0.9	
	0.900	0.8	
	1.000	0.7	
1-10 μg/ml Manifold (Figure 2)	2.000	2.5	(P=0.95, n=10)
	8.000	1.1	(P=0.95, n=9)

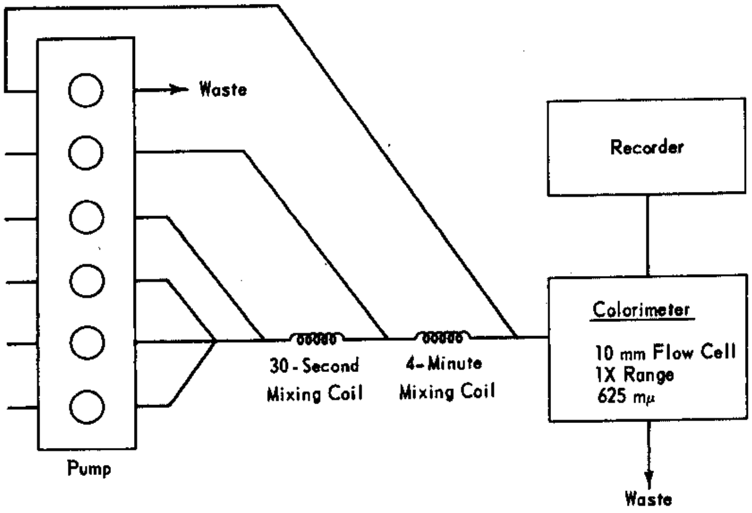
Reagent	Flow Rate, cc/minute
Air (out)	0.32
Air (in)	0.32
Color Reagent*	3.39
Sample	3.40
Sample	3.90



* Chelate of lanthanum and alizarin complexone

FIG. 1 FLOW DIAGRAM OF AUTOMATED FLUORIDE METHOD WITH THE 0.050 - 1 μg F⁻/ml MANIFOLD

Reagent	Flow Rate, cc/minute
Air (out)	0.32
Color Reagent*	2.42
Air (in)	0.32
Sample	0.32
Water	0.80
Water	2.50



* Chelate of lanthanum and alizarin complexone

FIG. 2 FLOW DIAGRAM OF AUTOMATED FLUORIDE METHOD WITH THE 1-10 μg F⁻/ml MANIFOLD

TABLE II

Interferences in Automated Fluoride Method

Ion	Maximum Tolerable Mole Ratio of Ion to Fluoride
NO_3^-	7,000
$SO_4^=$	700
Cl^-	10,000

SEPARATION OF FLUORIDE BY PYROHYDROLYSIS

The pyrohydrolysis procedure as reported by Warf was tested in the laboratory and found to be satisfactory for solids; however, when liquid samples were prepared according to Powell and Menis(10) and analyzed by Warf's pyrohydrolysis procedure, fluoride recoveries of only 70-90% were obtained.

Quantitative recovery was obtained by two modifications of the preparation and pyrohydrolysis steps for liquid samples. In the modification of the preparation step, the liquid sample and the sodium hydroxide used for neutralization were both absorbed onto U_3O_8 accelerator in a platinum boat. Next, a layer of saturated aluminum nitrate solution was added, and the boat and its contents were dried for one hour in an oven at 110°C. It is postulated that any hydrogen fluoride released by the sample during drying is retained by the aluminum until the high temperatures attained during pyrohydrolysis are reached.

In the second modification, the steam used for pyrohydrolysis was enriched with oxygen. Since oxygen enrichment was necessary for quantitative recovery of fluoride from liquid samples, it seems likely that oxygen serves a more fundamental purpose than simply as a sweep gas as indicated by Powell and Menis. The role of oxygen is more readily explained by Equation 2 (see Introduction).

The conditions used for preparation of samples and for the pyrohydrolysis are:

1. Solid samples were prepared for pyrohydrolysis by mixing them thoroughly with 0.4 g of U_3O_8 in a platinum boat. For UO_2 samples containing trace amounts of fluorides, 5 g samples were used. For other materials analyzed, the maximum weight of fluoride in the sample was 18 mg.

2. Liquid samples were prepared for pyrohydrolysis as follows:

   a. 0.4 g of U_3O_8 was spread evenly over the bottom of the platinum boat.

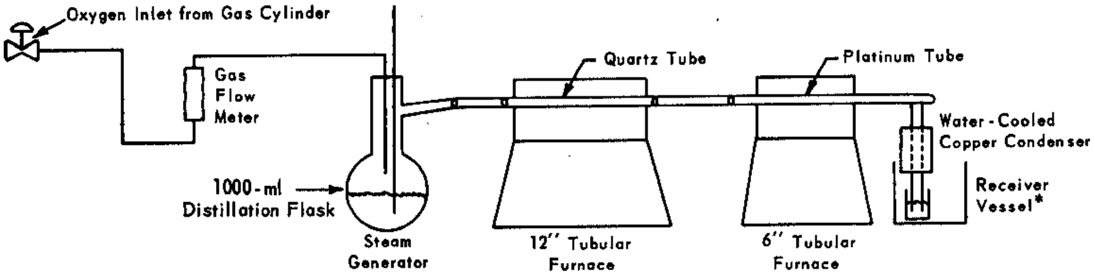
   b. An aliquot (<1 ml) of liquid sample was pipeted onto the U_3O_8.

   c. Sodium hydroxide solution (100 µl of 0.05N NaOH) was added to neutralize any acid. Higher concentrations of sodium hydroxide were used for highly acidic solutions.

   d. A one ml aliquot of saturated aluminum nitrate solution was spread evenly over the contents of the platinum boat to complex fluoride and prevent its volatilization during drying.

   e. The boat and contents were dried at 110°C for one hour.

3. In the pyrohydrolysis of all samples, the superheated steam was enriched with oxygen. The rate of steam generation was such that approximately 180 ml of condensate was collected in the hour used for the pyrohydrolysis. The oxygen flow was approximately 0.5 standard liters per minute. During pyrohydrolysis, the steam was heated to 900°C, while the sample was heated to 1100°C. A diagram of the pyrohydrolysis apparatus is shown in Figure 3.



*50-ml polyethylene beaker (to hold the 25 ml of 0.1 M NaOH) inside of a 250-ml polyethylene beaker.

FIG. 3 PYROHYDROLYSIS EQUIPMENT

4. The sample, prepared in a platinum boat as noted above, was placed in the platinum tube furnace at room temperature. After a normal flow of oxygen-enriched steam was obtained, the steam was allowed to pass over the sample, and the platinum tube furnace was then heated to 1100°C.

5. The hydrogen fluoride was absorbed in 25 ml of 0.1N NaOH solution.

6. After one hour, the pyrohydrolysis was discontinued. The combined condensate and sodium hydroxide absorbent solution was adjusted to a pH of 6-7 (phenolphthalein indicator) and was diluted to 250 ml prior to analysis for fluoride by the automated colorimetric method.

Since sodium fluoride is one of the most difficult fluorides to hydrolyze, it was used as the test material. On standards of solid sodium fluoride, 18-mg portions were analyzed by the combined pyrohydrolysis-colorimetric method. The average recovery was 100.3% with a precision of 0.9% ($P = 0.95$, $n = 12$). With standard aqueous solutions of sodium fluoride, a precision of 36% ($P = 0.95$, $n = 6$) was obtained at the detection limit of 25 µg, and a precision of 1% ($P = 0.95$, $n = 4$) was obtained with aliquots containing 475 µg of fluoride. A precision of 1% ($P = 0.95$, $n = 3$) was obtained on samples containing uranium, zirconium, and several milligrams of fluoride.

The method was used successfully to analyze uranium dioxide samples that contained less than 25 µg of fluoride per gram of sample.

APPENDIX

REAGENTS FOR COLORIMETRIC DETERMINATION

Analyzed reagent-grade chemicals and distilled water were used in the preparation of all reagents.

1. Alizarin Complexone (Alizarin Fluorine Blue from Hopkin and Williams Ltd, Chadwell Heath, Essex, England)

2. Ammonium Hydroxide, Conc

3. Ammonium Acetate, 20% w/v (prepared in H_2O)

4. Sodium Acetate, Anhydrous

5. Acetic Acid, Glacial

6. Acetone

7. Lanthanum Oxide

8. Color Reagent - Dissolve 0.0480 g of alizarin complexone in 0.1 ml of concentrated ammonium hydroxide, 1 ml of 20% w/v ammonium acetate, and 2 ml of water. Filter the solution through Whatman #1 Filter Paper into a 200-ml volumetric flask containing 8.2 g of anhydrous sodium acetate dissolved in 6.0 ml of glacial acetic acid and 10-20 ml of water. Wash the filter paper with small amounts of water. Add 100 ml of acetone slowly while swirling. Add a solution prepared by dissolving 0.0410 g of lanthanum oxide in 2.5 ml of 2M HCl with gentle heating. After mixing, dilute to nearly 200 ml, cool if necessary, and dilute to volume. Mix well. The reagent is stable approximately one week.

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by D. E. Harrington and R. S. Dorsett

Suitable analytical methods have not been available for the routine determination of fluoride in materials of interest in the nuclear industry. The principal problem in the analysis stems from the tendency of fluoride to form complexes that are difficult to separate from interferences and to measure by conventional techniques. Many analytical methods have been published, but these methods are applicable to only a narrow range of sample matrices. Consequently, considerable time was required in evaluating the method of analysis for each new type of sample.

Harrington and Dorsett have provided a general method that is applicable to the wide variety of samples that we encounter, even those high in complexing agents such as aluminum, zirconium and uranium. Because of its broad application, this method has permitted us to place fluoride analyses in the routine category.

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December 28, 1965

Mr. R. G. Erdley, Chief
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Post Office Box A
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Dear Mr. Erdley:

REQUEST FOR PATENT REVIEW

Please review for patent matter:

DP-1004, "Determination of Fluoride by Pyrohydrolysis and Automated Colorimetry", by D. E. Harrington and R. S. Dorsett.

If any technical clarification is needed please call J. E. Beach whose document review is attached.

Please telephone your comments to the TIS Office (Ext. 3402) and notify me by signing and returning to TIS the original of this letter. A copy is provided for your file.

If you decide to pursue a patent on any development covered, I shall be happy to supply additional information required such as appropriate references and the names of persons responsible for the development.

The above item is approved
for release.

R G Erdley 1-4-66
R. G. Erdley, Chief Date
Patent Branch
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Very truly yours,

C. W. J. Wende, Director
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By: J E Beach
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BETTER THINGS FOR BETTER LIVING . . . *THROUGH CHEMISTRY*

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