ARH-SA-96

CONF-710658--2

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Fluoride Separation by Microdiffusion and Determination by Fluoride Specific Ion Electrode

William I. Winters

June, 1971

Atlantic Richfield Hanford Company
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CONF-710658--2

FLUORIDE SEPARATION BY MICRODIFFUSION AND DETERMINATION
BY FLUORIDE SPECIFIC ION ELECTRODE

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June 1971

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To be presented at the

26th Northwest Regional American Chemical Society Meeting
June 16, 17, and 18, 1971
Bozeman, Montana

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ABSTRACT

Microdiffusion was found to be a fast and convenient method for separating trace quantities (2 μ g) of fluoride from nuclear processing solutions. The tolerance levels for 17 interfering elements were studied including uranium and thorium. Both sulfuric and phosphoric acids were investigated as distillation mediums. The acceleration effect of hexamethyldisiloxane as a fluoride carrier was also determined. When used in conjunction with the fluoride specific ion electrode, the technique offers several advantages over other distillation, pyrohydrolysis, and spectrophotometric techniques.

- *Smaller quantities of fluoride may be separated.*
- *A large number of samples may be analyzed at one time.*
- *The method requires less training and is less subject to operator errors and operating parameters.*
- *The diffusion apparatus is disposable, therefore eliminating the need for expensive apparatus and decontamination of equipment.*
- *The method is adaptable to glove box and hot cell operations.*

FLUORIDE SEPARATION BY MICRODIFFUSION AND DETERMINATION
BY FLUORIDE SPECIFIC ION ELECTRODE

INTRODUCTION

The fluoride ion is widely used in the nuclear fuel re-processing industry (e.g., the dissolution of Zircalloy*-clad nuclear fuels). Because of the corrosive nature of fluoride, its concentration must be carefully monitored throughout reprocessing and waste handling to ensure that the integrity of the stainless steel tanks is being maintained and that product specifications are being met.

Nuclear processing solutions containing the fluoride ion also normally include significant amounts of numerous cations; therefore fluoride requires separation prior to determination. The separation processes of distillation and pyrohydrolysis have been used in the past with limited success. Both of these methods require relatively high volumes for trapping fluoride, expensive equipment which is difficult to decontaminate, and careful control of operating parameters for successful analysis. Because of these problems, it was desirable to investigate a different fluoride separation technique which would be more adaptable to the nuclear processing solutions.

As early as 1939 Edward J. Conway⁽¹⁾ used microdiffusion for separating trace quantities of volatile compounds from biological materials. More recently Hey and Jenkins⁽²⁾ have used the technique to determine fluoride in river water. Because of the simplicity of the procedure, it was decided

* Trade name, Zirconium Company of America.

to investigate microdiffusion as a possible alternative to distillation and pyrohydrolysis from nuclear processing solution.

SUMMARY AND CONCLUSIONS

A rapid, simple method for the determination of fluoride in the presence of numerous cations found in nuclear processing solutions was developed. The fluoride is separated from cationic interferences by using the microdiffusion technique, in which the fluoride is diffused from an $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$ matrix at 65 °C into a 2.0M NaOH collecting medium using a two-compartment microdiffusion dish (Figure 1). The separated fluoride is then determined by specific ion electrode.

The sensitivity of the method is governed by the impurities in the reagents, particularly H_3PO_4 , and by the linearity of the electrode response. The fluoride electrode provides a linear response to approximately $2 \times 10^{-6} \text{ M F}$. Contamination from one milliliter of the $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$ acid matrix yields 1.0×10^{-5} millimoles of fluoride. Two micrograms of fluoride may be separated and determined in this procedure with a precision of ± 5.0 percent. Smaller quantities of fluoride would result in a further loss of precision. Sample sizes in the microdiffusion dish used are limited to 1 ml or less. Attempts to purify reagents by distillation and washing with hexamethyldisiloxane were only partially successful.

Twenty-nine elements were found not to seriously interfere (at least 85 percent recovery) at a 100:1 mole ratio of the element to fluoride. The method was also successfully applied to the determination of fluoride in 1 molar uranium and thorium nitrate solutions. The use of a 2M NaOH collecting medium and a 50 percent total ionic strength buffer allows up to two milliequivalents of volatile acids (HCl , HNO_3) to be present without causing an interference. This feature makes

the method adaptable to the acid samples from nuclear processing solutions. Studies using hexamethyldisiloxane (HMDS) indicated that no significant advantages resulted using HMDS when the microdiffusion dishes are heated at 65 °C for two hours or longer. The method described uses an overnight heating time even though shorter heating times appear feasible. Actual analysis time requiring a technician is about one-half hour per sample when analyzed in 12-sample lots.

The microdiffusion separation and specific ion determination of fluoride offers a sample and versatile method with several advantages over normal pyrohydrolysis, distillation, and spectrophotometric techniques.

- The fluoride may be collected in a smaller volume of trapping solution (1 ml compared with 20 ml or more), allowing smaller sample sizes to be used.
- A large number of samples may be analyzed at one time without duplication of expensive equipment.
- The separation of fluoride from metals is, in most cases, as good as or better than other techniques.
- The method requires few manipulations and therefore requires less training and is less subject to operator errors than other techniques.
- The fluoride apparatus is disposable, therefore eliminating the need for expensive apparatus and decontamination of equipment.
- Using the specific ion electrode, there is no interference from trace quantities of phosphate.
- The method is easily adaptable to cubicle or glove box operations.

EXPERIMENTAL

APPARATUS

Microdiffusion dishes: Falcon plastic microdiffusion dish, 7004, 65 x 15 mm (Falcon Plastics).

pH meter: Orion Model 801 pH meter with an Orion Model 851 digital printer system (Orion Research, Inc.).

Fluoride specific ion electrode: Orion Model 94-09 (Orion Research, Inc.).

Drying oven must be capable of maintaining a constant 65 °C temperature.

All volume measurements were made using glass pipets and flasks. Polyethylene bottles were used to store distilled fluoride samples after the final volume measurement. Disposable 30-ml plastic beakers were used to contain the sample during specific ion measurement. Teflon*-coated steel stir bars were used for all stirring operations.

REAGENTS

Distillation medium: 50 vol% mixture of 70 vol% H_2SO_4 and H_3PO_4 acids.

Trapping medium: $2.00 \pm 0.05M$ NaOH (stored in polyethylene).

Nitric acid: $4.00 \pm 0.05M$ HNO_3 .

Dow Corning silicone stopcock grease.

Total Ionic Strength Adjustable Buffer (TISAB) - Orion No. 94-09-09 (Orion Research, Inc.).

Fluoride standard: $0.100M$ NaF (stored in polyethylene bottles).

* Trade name, duPont Company.

GENERAL DESCRIPTION

Microdiffusion has been extensively used by Edward J. Conway⁽¹⁾ to separate and determine numerous compounds and elements from biological samples. In the following procedure, attempts have been made to optimize the parameters of microdiffusion to allow fluoride separation from radioactive aqueous solutions of inorganic cations.

MICRODIFFUSION DISH PREPARATION

Disposable plastic microdiffusion dishes as illustrated in Figures 1 and 2 were used to simplify the handling of radioactive materials. The dishes are prepared by placing silicone grease along the outside edge of the lid. This prevents the fluoride from escaping as gaseous HF when the sample and acid are mixed and the dish is heated. Additional silicone grease is used to coat the outside wall of the inner compartment (Figure 2, B-1). This helps prevent wetting of the wall by the acid matrix which may lead to acid and sample being carried over into the center compartment. If acid were carried over into the center compartment, the NaOH would be neutralized and incompleting trapping of diffused HF would occur. Silicone grease (Figure 2, B-2) is also used to separate the outside compartment into two sections (Figure 2, C and D)--one for the sample and one for the acid. This prevents mixing before the dish can be sealed, thereby reducing the possibility of HF escaping and giving low results.

SAMPLE INTRODUCTION AND DIFFUSION AND PREPARATION

One milliliter of 2.0M NaOH is placed in the center compartment. The sample is pipetted into one of the sections of the outer compartment. Sample sizes are limited to 1 ml. Larger sample sizes would result in the acid being spilled over

MICRODIFFUSION DISH

- A. $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ -SAMPLE (OUTER COMPARTMENT)
- B. 2.0M NaOH - TRAPPING SOLN (INNER COMPARTMENT)
- C. LID
- D. SILICONE GREASE SEAL

FIGURE 1

MICRODIFFUSION DISH

TOP VIEW - MICRODIFFUSION DISH

- A. PLASTIC DIVIDER
- B₁. SHADED AREA - AREA COATED WITH LAYER OF SILICONE GREASE TO PREVENT WETTING OF INNER COMPARTMENT WALL
- B₂. FORMS TWO CELLS - ONE FOR SAMPLE AND ONE FOR $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$ TO PREVENT MIXING BEFORE LID IS PLACED ON.
- C. SAMPLE SECTION
- D. ACID SECTION

FIGURE 2

TOP VIEW - MICRODIFFUSION DISH

into the center compartment. The $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$ mixture is then pipetted into the other section of the outer compartment. Two milliliters of acid matrix are used for sample sizes less than 500 μl . One and one-half milliliters of the acid matrix are used for sample sizes up to 1 ml. The lid is then placed on the dish and sealed by turning. The sample and acid are mixed by tilting and rotating on a flat surface. The dish is then placed in a drying oven at 65 °C for overnight. The next day the lids are removed and the center compartment contents transferred to a 10-ml volumetric flask containing 5 ml of TISAB buffer with two 2-ml portions of de-ionized H_2O . The pH is then adjusted with 0.5 ml of 4.0M HNO_3 and the flask brought to mark. The contents of the flask are stirred with a Teflon stir bar and then transferred to a plastic beaker for fluoride determination with the specific ion electrode. A more detailed description of the procedure is given in the Appendix (A-1).

CHEMICAL BASIS

The chemical basis for the procedure is simple. When the fluoride in the sample comes in contact with the $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ acid, it forms HF which is volatilized and collected in the center NaOH compartment

However according to Taves,⁽³⁾ the silicone grease is a necessary ingredient for fluoride volatilization since it provides volatile fluorosilanes which hydrolyze in the NaOH to yield NaF. A mechanism using hexamethyldisiloxane (HMDS) is proposed by Taves⁽³⁾ as follows:

The high concentration of sulfate and phosphate aid in freeing the fluoride from metallic complexes by forming new, stronger complexes.

DIFFUSION MATRIX STUDIES

Hey and Jenkins⁽²⁾ used 70 vol% H_2SO_4 as a diffusion matrix in their studies and 0.5N NaOH as a collecting medium. Initial tests using this system resulted in incomplete recovery of 10^{-3} fluoride from 0.1M Zr and 400 g/liter uranium solutions. This acid also formed gelatinous precipitates with thorium and zirconium which tended to cause the acid matrix to spill-over into the center compartment. A phosphoric acid and a 50% mixture of phosphoric and sulfuric acids were investigated as alternatives for H_2SO_4 . Both of these matrices gave high percent recoveries but reduced the large volume of hydrous precipitate. The high yields were later explained by a fluoride contamination of about $1.5 \times 10^{-5} \text{M}$ HF in the phosphoric acid. The mixture of the H_3PO_4 - H_2SO_4 was chosen for several reasons:

- It gave the best consistent recoveries of fluoride.
- The mixture of $\text{SO}_4^{=}$ and $\text{PO}_4^{=}$ as complexing ions was more suitable for a large number of cations.
- The precipitate formed with many cations (Ba, U, Th, Zr) was not as voluminous and hydrous as in H_2SO_4 , and resulted in fewer reruns.

The primary disadvantage of the H_2SO_4 - H_3PO_4 matrix is the fluoride contamination from H_3PO_4 . The error caused by contamination must be corrected by running blanks for the reagents and subtracting the fluoride in the blank from the final result. This contamination also limits the detection limits as will be discussed later.

It was also discovered that in analyzing highly acid samples, one milliliter of 0.5M NaOH was not sufficient to

maintain a basic collecting medium. A 2.0M NaOH was chosen since it allowed samples containing up to 2 milliequivalents of acid to be used without adversely affecting the TISAB buffer, and did not form a salt cake along the inside of the center compartment as frequently occurred with higher normalities of NaOH. This salt cake may result in acid being carried into the center compartment. Higher concentrations of NaOH will be necessary if more than 2 milliequivalents of acid are in the sample. An appropriate acid adjustment will be necessary to ensure the pH of the TISAB buffer is between 4.5 and 6.0.

HEXAMETHYLDISILOXANE (HMDS) ACCELERATOR STUDIES

According to Taves,⁽³⁾ HMDS may be used to reduce the time necessary to diffuse the fluoride from the acid to the caustic compartment. Taves' method is carried out at room temperature with constant mixing of the dish by rotation. In Taves' procedure, 6M HCl solution saturated with HMDS is added through a small hole in the repositioned lid.

The effect of HMDS in our work was studied by directly adding 100 μ l of HMDS to the outside compartment of the micro-diffusion dish after addition of the sample and before addition of the acid. A 500 μ l sample of an 0.010 NaF standard and 500 μ l of a $10^{-3}M$ F^- and 0.1M Zr solution were then analyzed with and without HMDS over a four-hour time period in a 65 °C drying oven. Results of these tests are shown in Tables I and II.

These data indicate that HMDS when applied in the described manner may have a significant advantage during the first hour of diffusion; however after two hours, the acceleration effect and advantages of HMDS are questionable. Further studies in which HMDS was used with cations (Cd, Ca, Mo, Sr) in acid solutions resulted in low percent recoveries for fluoride. When HMDS was omitted, recoveries returned to normal. It may be proposed that the HMDS was causing the fluoride to diffuse

TABLE I

THE ACCELERATION EFFECT OF HEXAMETHYLDISILOXANE
ON THE DIFFUSION OF AN NaF STANDARD

<u>Time</u> <u>hr</u>	<u>Without HMDS</u>		<u>With HMDS</u>	
	<u>mV</u>	<u>% Recovered</u>	<u>mV</u>	<u>% Recovered</u>
0.5	42.3	69.2	37.1	84.8
1.	37.2	84.4	35.5	90.4
2.	37.6	83.2	35.5	90.5
4.	42.8*	67.8	35.1	91.8

* Center was acid resulting in low recovery.

TABLE II

THE ACCELERATION EFFECT OF HEXAMETHYLDISILOXANE
ON THE DIFFUSION OF AN 0.1M Zr-0.002M F⁻ SOLUTION

<u>Time</u> <u>hr</u>	<u>Without HMDS</u>		<u>With HMDS</u>	
	<u>mV</u>	<u>% Recovered</u>	<u>mV</u>	<u>% Recovered</u>
0.5	96.1	85.8	93.8	94.0
1.	95.2	88.8	93.8	94.0
2.	93.3	95.8	95.2	88.8
4.	93.8	94.0	Spilled	Spilled

before the lid could be placed on and sealed. Since there was no need for a fast turn-around time for results, and since low percent recoveries resulted with certain cations, HMDS was not used in this method. For applications where fast analyses are needed, the technique described by Taves may merit further consideration.

INTERFERENCE STUDIES

Since nuclear processing solutions may contain a wide variety of cations at different concentrations, it was desirable to know the effect of many of these cations on the diffusion

of fluoride in our procedures. This study was made by preparing a solution of the cation and a known amount of fluoride. In most cases a mole ratio of $0.1M$ cation/ $0.001M$ F^- was used since the concentration of most of the cations of interest are not expected to exceed $0.1M$. The concentration of fluoride was chosen so that the final concentration after separation and preparation was high enough that any effects due to contamination or loss of fluoride to walls of a container were minimal. Even at this concentration the results of $100\ \mu l$ aliquots ($2\ \mu g$ fluoride) had to be corrected by a normalizing factor of 1.15 for contribution due to fluoride in the blank. Aliquots of $500\ \mu l$ ($10\ \mu g$ fluoride) required a correction of only 1.03.

Samples containing cations which form insoluble fluorides such as La had to be analyzed immediately after makeup and could not be used after setting over a day. For U and Th, a 1000:1 mole ratio was used for the interference study. In these particular cases, the preparation of a true fluoride standard became difficult due to the natural fluoride contamination in the high-grade uranium oxide and in the reagent-grade thorium nitrate used to make the standards. Fluoride contamination in these materials as analyzed by this method was $14.8\ pF^-/mpU$ and $2.0\ pF^-/mpTh$. Results of interference studies on these two elements is expressed as the percent recovery of the sum of the fluoride due to reagent blank, the fluoride spike, and the fluoride naturally occurring in the uranium as determined by this procedure. Results shown in Table III were done with $500\ \mu l$ sample sizes of the cation-fluoride standard. Smaller sample volumes ($\leq 100\ \mu l$) normally resulted in better percent recoveries.

BUFFER STUDIES

Before the separated fluoride could be analyzed by specific ion electrode, it was necessary to adjust the pH of the caustic center compartment to a value between about 4.5 and $6.0^{(4)}$ in order to avoid a negative interference from too low a pH or a

TABLE III
CATION INTERFERENCE STUDIES

Cation	Cation Concentration	Fluoride Concentration	Sample Size	% Recoveries
	<i>M</i>	<i>M</i>	μl	
Ag	0.01	1×10^{-3}	500	92.7
Al	0.10	1×10^{-3}	500	96.0
B	0.10	1×10^{-3}	500	94.8
Ca	0.10	1×10^{-3}	500	97.6
Cd	0.10	1×10^{-3}	500	94.8
Co	0.02	1×10^{-3}	500	87.2
Cr	0.10	1×10^{-3}	500	97.6
Cu	0.02	1×10^{-3}	500	94.9
Fe	0.10	1×10^{-3}	500	88.9
Hg	0.05	1×10^{-3}	500	98.2
La	0.07	1×10^{-3}	500	91.4
Mn	0.10	1×10^{-3}	500	88.9
Mo	0.10	1×10^{-3}	500	93.6
Ni	0.02	1×10^{-3}	500	97.2
Pd	0.01	1×10^{-3}	500	88.9
Pb	0.05	1×10^{-3}	500	94.5
Ru	0.01	1×10^{-3}	500	99.4
Sb	0.01	1×10^{-3}	100*	100.0
Si	0.01	1×10^{-3}	500	91.0
Sn	0.01	1×10^{-3}	500	87.9
Sr	0.01	1×10^{-3}	500	97.6
Th	1.0	1×10^{-3}	500	92.3
Ti	0.10	1×10^{-3}	500	96.3
U	1.0	1×10^{-3}	500	87.7
W	0.05	1×10^{-3}	500	98.0
Y	0.10	1×10^{-3}	500	92.7
Zn	0.02	1×10^{-3}	500	97.4
Zr	0.10	1×10^{-3}	500	89.4

* The standard contained too high a concentration of HCl for 500 μl sample size.

positive interference from too high a pH. A constant ionic strength is also desirable to ensure reproducible results from sample to sample. The effect of varying pH, ionic strength, and other factors affecting the specific ion electrode are discussed in the instruction manual for the electrode.⁽⁴⁾ In order to maintain simplicity, a buffer was required that would

be capable of adjusting the pH of 1 ml of 2M NaOH between 4.5 and 6.0, and provide a constant ionic strength without the need for a pH measurement or additional acid. The total ionic strength adjustment buffer (TISAB) of Orion and a 4M potassium acetate buffer were investigated for this purpose.

During the test of these buffers it was discovered that the concentration of the buffer affected the range of linearity for the electrode. The more concentrated the buffer, the faster the linearity drops off as lower concentrations of fluoride are approached. This may best be illustrated in Figure 3. The magnitude of the effect is seen in the difference in the millivolts between successive points or the change in slope, as shown in Table IV.

TABLE IV
BUFFER EFFECT ON CALIBRATION CURVE
OF FLUORIDE ELECTRODE

F ⁻ Concentration M	Difference in mV Between Successive 10 ⁻ⁿ M F ⁻				
	Deionized H ₂ O mV	50% TISAB mV	10% KAc mV	20% KAc mV	50% KAc mV
10 ⁻⁷					
10 ⁻⁶	42.4	-	-	-	-
10 ⁻⁵	57.7	52.9	41.3	36.5	25.0
10 ⁻⁴	58.9	58.9	57.3	56.0	51.7
10 ⁻³	58.9	59.1	59.1	59.0	58.3

The other factor considered in the choice of the buffer was its strength or the amount of acid or base a given quantity of buffer could tolerate and still maintain the necessary pH. The tolerance of these buffers in terms of milliequivalents of acid and base are shown in Table V.

FIGURE 1
BUFFER EFFECT ON FLUORIDE CALIBRATION

TABLE V
ACID-BASE TOLERANCE LEVELS
OF BUFFERS USED WITH FLUORIDE ELECTRODE

<u>Buffer</u>	<u>meq H⁺</u>	<u>meq OH⁻</u>
50% TISAB	1.8	0.4
50% 4M KAc	2.0	4.0
20% 4M KAc	-	2.4

From these two sets of data the following conclusions may be drawn:

- A 20% 4M potassium acetate buffer may be used without further pH adjustment if the final concentration of fluoride is greater than $2 \times 10^{-5}M$.
- A 50% TISAB buffer may be used with the addition of an equivalent amount of acid (2 meq for 1 ml of 2M NaOH) if the final fluoride concentration is greater than $2 \times 10^{-6}M$.

The TISAB buffer was chosen for our work because of the extended linearity range. Using this buffer, it is possible to tolerate samples containing up to 2 milliequivalents of acid.

During the time studies with HMDS, the pH of the final solution was found to decrease with longer diffusion times in the oven. This indicated that a larger proportion of the volatile acid in the sample was being diffused with time. Shorter diffusion times and lower diffusion temperatures could allow a greater tolerance of acid in samples, if needed.

BLANK STUDIES AND DETECTION LIMITS

The ability to measure the true detection limits of the method and the precision at these fluoride levels is determined by the amount of fluoride in the blank and one's ability

to measure this amount. In order to improve the detection limits and improve the precision of making measurements at low concentrations, two attempts were made to reduce the fluoride in the $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ matrix.

Attempts to distill the fluoride from the acid matrix by adding H_2O and then boiling the water off were only partially successful. This technique resulted in the reduction of fluoride from $7.5 \times 10^{-6} \text{M F}^-$ to $4.5 \times 10^{-6} \text{M F}^-$ in the acid matrix. Hexamethyldisiloxane was used in an attempt to purify both the acid mixture and a 400 g/liter uranium standard. The HMDS was emulsified with the reagents at a 1:10 ratio (HMDS/reagent) and then stirred vigorously for two hours. The remaining unvolatilized HMDS was removed by stirring and heating at a low temperature. Essentially no improvement was noticed in the acid matrix, but the fluoride in the uranium was reduced from $3.72 \times 10^{-4} \text{M}$ to $9.12 \times 10^{-5} \text{M}$. Even though the amount of fluoride in the reagents was reduced, the decrease was not significant enough to allow the determination of fluoride without a blank correction. Two micrograms of fluoride may be separated and determined with only a 15 to 20% correction due to the fluoride in the blank. In order to lower the detection limit to 0.2 μg fluoride, a 150% blank correction would be required which would result in significantly poorer precision. The area of reagent purification merits further consideration if lower detection limits are required.

CALIBRATION AND CALCULATIONS

Calibration curves were prepared by making the necessary dilutions of a standard NaF solution into a final volume (normally 250 ml) which was 50 vol% in TISAB buffer and 0.2M in NaNO_3 . The NaNO_3 was added to compensate for any changes in ionic strength due to the neutralization of 2 milliequivalents of NaOH. Calibrations were initially prepared from 10^{-3}M fluoride to 10^{-6}M fluoride for any electrode system. Day-to-day

calibrations were then made using three points ($10^{-3}M$, $10^{-4}M$, and $10^{-5}M F^{-}$). Intercept changes were corrected using the relative millivolt control of the meter so that millivolt readings were identical with the initial calibration. The inability to reproduce the initial calibration indicated poor standard or changes in the electrode response, which affected the slope. All standards should be stored in clean, polyethylene bottles for extended shelf-life.

The three standards used each day were measured before and after analysis of the samples. The millivolt readings from these standards were then averaged and a "least squares" regression curve of the natural logarithm of concentration as a function of the millivolt reading was calculated. The calculation for the natural logarithm of the sample fluoride concentration could then be calculated using an equation of the following form:

$$\ln(c) = \text{millivolts} + \text{intercept} \left(\frac{1}{\text{slope}} \right)$$

By using a programmable Olivetti calculator (Olivetti Underwood Corporation) for least square calculations and a Wang calculator (Wang Laboratories, Inc.) for logarithms, the errors and time involved in plotting and graphical interpretation were eliminated.

ACCURACY AND PRECISION

The accuracy and precision of the method depends on the type of sample being analyzed with respect to the amount of fluoride in the sample and blank, the required sample size, and the concentration of the interfering ions.

Table VI shows the results obtained at various levels of fluoride and in different matrices.

The standard deviations given in Table VI are calculated at the 95% confidence level based on 10 pieces of data. The

TABLE VI
ACCURACY AND PRECISION RESULTS

Sample	Sample Size		Molarity $\bar{x} \pm$ Standard Deviation	% Recovery $\bar{x} \pm$ Standard Deviation
	μ l	F ⁻ μ g		
$1 \times 10^{-5}M$ NaF	1000	0.19	$1.09 \pm 0.13 \times 10^{-5}$	109.1 ± 12.5
$1 \times 10^{-4}M$ NaF	1000	1.9	$0.97 \pm 0.05 \times 10^{-4}$	97.3 ± 4.9
AR001	100	8.6	$4.44 \pm 0.12 \times 10^{-3}$	97.6 ± 2.7
^{191}Th , g/liter	500	0.57	$5.96 \pm 0.20 \times 10^{-5}$	± 3.3
Th + $10^{-3}M$ F ⁻	500	10.	$0.92 \pm 0.28 \times 10^{-3}$	91.9 ± 2.8
^{240}U , g/liter	500	2.2	$2.36 \pm 0.22 \times 10^{-4}$	± 9.3
U + $10^{-3}M$ F ⁻	500	12.	$0.86 \pm 0.38 \times 10^{-3}$	86.1 ± 3.8

results for the Th plus $10^{-3}M$ fluoride spike and the U plus $10^{-3}M$ fluoride spike are based on the spike recovery after subtracting out the fluoride concentration due to the H_2SO_4 - H_3PO_4 blank and the fluoride contamination in the uranium and thorium standards.

In all the standards except the $1 \times 10^{-5}M$ NaF, the results are biased low which might be expected due to incomplete diffusion in a complicated matrix. The high percent recovery and largest standard deviation of the $1 \times 10^{-5}M$ NaF standard can be explained by the fluoride contamination in the blank approaching the same concentration as the standard.

The AR001 standard is a synthetic nuclear waste solution. The composition of this feed is shown in Table VII.

Even though the results indicate that the method is biased low for most matrices, it is adequate for process applications. The precision of the method could be improved by operating with a lower or negligible blank. Other methods of fluoride measurement such as titrimetry or spectrophotometry might improve the precision only at the sacrifice of speed and

TABLE VII
CONTENTS OF AR001 SYNTHETIC STANDARD

Ion	Concentration
	<i>M</i>
Al	0.351
Mg	9.89×10^{-4}
Cd	1.03×10^{-3}
Ca	1.29×10^{-3}
Ba	5.55×10^{-4}
Cr	1.93×10^{-2}
Ni	1.20×10^{-2}
Mn	2.93×10^{-3}
Sr	5.49×10^{-4}
Zr	2.81×10^{-3}
La	1.11×10^{-3}
Fe	0.308
Na	0.554
F ⁻	4.55×10^{-3}
Nitric acid	1.90

simplicity. These data illustrate that microdiffusion can separate trace quantities of fluoride from numerous cations and suggest that the technique may be useful for other separations such as chloride where distillation or pyrohydrolysis have previously been used.

REFERENCES

1. Edward J. Conway. "Microdiffusion Analysis and Volumetric Error," Crosby Lockwood and Son, Ltd., London (1962).
2. A. E. Hey and Jenkins. "Determination of Fluorine by Microdiffusion as Applied to Waste Waters, River Samples, and Effluents," Water Research, vol. 3, pp. 901-906. Pergamon Press, 1969.
3. Donald R. Taves. "Separation of Fluoride by Rapid Diffusion Using Hexamethyldisiloxane," *Talanta*, vol. 15, pp. 969-974, 1968.

4. Orion Instruction Manual for the Model 94-09 Fluoride Electrode, Form 1794-09/768, 1967. Orion Research, Inc., 11 Blackstone Street, Cambridge, Massachusetts 02139.

APPENDIX

APPENDIX

DETAILS FOR THE METHOD FOR THE DETERMINATION OF FLUORIDE
BY MICRODIFFUSION SEPARATION AND SPECIFIC ION MEASUREMENTAPPARATUS

Falcon plastic microdiffusion dishes, 7004, 65 x 10 mm
(Falcon Plastics).

Orion Research, Inc. Model 801 pH meter.

Orion Model 94-09 fluoride specific ion electrode.

Orion Model 90-01 single junction reference electrode.

Drying oven.

REAGENTS

Distillation medium: 50% mixture of 70 vol% H_2SO_4 and
70 vol% H_3PO_4 .

Trapping medium: $2.00 \pm 0.05M$ NaOH.

Nitric acid: $4.00 \pm 0.05M$ HNO_3 .

Dow Corning Corporation silicone stopcock grease.

Total ionic strength adjustment buffer (TISAB) Orion
No. 94-09-09.

NaF: $0.100M$ stored in polyethylene.

Deionized water was used in making up reagents.

PROCEDURE

Procedure	Comment
1. Prepare a microdiffusion (MD) dish by filling the groove inside of the lid with silicone grease.	This may be done with a plastic disposable syringe using the plastic needle protector as a dispensing tip.
2. Smear silicone grease along the outside wall of the inside compartment and separate the outside compartment into two sections using a thin film of the grease (see Figure 2).	This helps to prevent the acid matrix from carrying over into the center compartment and keeps the sample and acid separated until the lid can be seated.
3. Pipet 1 ml of 2.0M NaOH into the center compartment of the MD dish.	
4. Pipet the sample into one section of the outside compartment of the MD dish.	Sample size should not be greater than 1 ml.
5. Immediately pipet 2.0 ml of H_2SO_4 - H_3PO_4 mixture into the other section of the outside compartment of the MD dish and cover the MD with its lid. Press and twist the lid to ensure a good seal. Mix the contents by turning on a flat surface or by carefully tilting from side to side.	a. For 500 μl sample sizes and larger, only 1.5 ml of the H_2SO_4 - H_3PO_4 mixture should be used. b. Immediate capping of the dish prevents the escape of HF.
6. Place the MD dish in a drying oven at 65 °C for overnight.	Be sure oven and MD dishes are level to prevent spills.
7. Remove the MD dishes from the oven and remove the lids by twisting.	Be careful not to spill acid matrix into center compartment.
8. Slurp the H_2SO_4 - H_3PO_4 matrix from the outside compartment.	

Procedure	Comment
9. Add 2 ml of deionized H_2O to the center compartment and swirl to mix.	The center may be dry without affecting the results of the procedure.
10. Add one drop of phenolphthalein indicator to the center compartment. The color of this solution should be red or pink.	If the center compartment does not turn red, it means that the NaOH has been neutralized by an H_2SO_4 - H_3PO_4 spill or carryover or that the sample contained more than 2 milliequivalents of volatile acid (HCl , HNO_3). The acid condition of the center compartment usually means all the fluoride was not trapped and therefore low recoveries will result. If the acid condition was due to high acid in the sample, then a higher molarity of NaOH must be used in the center compartment with a corresponding increase of acid added in Step 13.
11. Transfer the contents of the center to a 10-ml volumetric flask containing 5 ml of TISAB buffer.	Steps 9 through 14 should be done as rapidly as possible to avoid fluoride losses to the glass or atmosphere.
12. Repeat Steps 9 and 11 with another 2-ml portion of deionized H_2O .	
13. Pipet 500 ml of 4.0M HNO_3 into the flask. Bring the flask to volume immediately with deionized H_2O and stir using a Teflon stir bar.	
14. As soon as the flask contents are homogeneous, transfer the solution and the stir bar to a clean, 25-ml polyethylene bottle, and cap.	a. The solution and stir bar may be transferred to a 30-ml disposable plastic beaker if the specific ion measurement is going to be made immediately.

<u>Procedure</u>	<u>Comment</u>
	b. All solutions less than $1 \times 10^{-5} M$ should be analyzed that same day.

REAGENT BLANK

The concentration of F^- in the $H_2SO_4-H_3PO_4$ and other reagents was measured by following the above procedure using 500 μl of deionized H_2O as the sample. The blank was determined using the average of four determinations. A new blank value was determined whenever a new batch of reagent was introduced.

SPECIFIC ION ELECTRODE MEASUREMENTS

Different techniques exist for calibrating and making the specific ion measurement. Many of these techniques are discussed in detail in the manufacturer's instruction manual for the fluoride electrode. The following method describes the technique used in this study using an Orion 801 pH meter with printout capabilities, and an Orion Model 94-09 fluoride electrode and Model 90-02 double junction reference electrode.

ELECTRODE PREPARATION

Reference Electrode: saturated KCl solution was used for the inner electrolyte on the double junction electrode. A 10% KNO_3 solution was used as an electrolyte in the outer compartment of the electrode. The inner electrolyte level was always kept at least one inch above the outer electrolyte. The electrode was soaked in 50% TISAB buffer when not being used.

Sensing Electrode: the fluoride electrode was coated with a thin layer of silicone oil to improve its response time. Excess oil was removed with cotton swabs, being careful not to scratch the crystal surface. The electrode was then shaken like a thermometer to ensure no air bubbles existed in the inside filling solution. When not being used, the electrode was stored dry with a protective cap.

Both electrodes were allowed to equilibrate 15 minutes in a 50% TISAB buffer-deionized H_2O solution before analysis of samples.

CALIBRATION

A calibration was prepared covering a range of $10^{-3}M$ to $10^{-6}M$ fluoride by pipetting the necessary aliquots of standard NaF into 250 ml flasks containing 125 ml of TISAB buffer and 50 ml of $1M$ $NaNO_3$. The flasks are brought to mark, stirred, and transferred to polyethylene bottles as rapidly as possible. The lower concentrations, less than $10^{-5}M$, are probably not stable for more than a few days.

The electrodes were washed with deionized H_2O and blotted dry with Kim-Wipes (Kimberly-Clark Corporation) or cotton swabs. The electrodes were then placed in the most dilute standard and its potential measured to the nearest ± 0.1 millivolt (mV). Extremely low concentrations less than $1 \times 10^{-5}M$ sometimes required up to 30 minutes for stabilization of millivolt reading. Millivolt readings were printed out every 0.5 minutes. A reading was considered stable if it did not change in three successive readings by more than ± 0.1 mV. Increasing concentrations of fluoride were measured following the deionized water wash and blot dry steps. Using this buffer system, a linear plot of millivolts versus the logarithm of concentration exist to $2 \times 10^{-6}M$ fluoride. The data were plotted on semi-log paper and a least square reduction of all linear data was calculated.

SAMPLE MEASUREMENT

The electrodes were prepared in the same manner as in the calibrations. Before measuring the potential of the samples, the calibration was checked using three standards: $10^{-3}M F^{-}$, $10^{-4}M F^{-}$, and $10^{-5}M F^{-}$. The instrument was set up on the $10^{-5}M F^{-}$ standard by adjusting the relative (mV) control of the meter until the same (mV) as the calibration was obtained. The other two standards were then checked for linearity. If they were not linear and did not agree with the original calibration, new standards and calibrations were prepared. The electrodes were placed in the 50% TISAB-deionized H_2O equilibrating solution after measuring the highest concentration for more dilute samples. The potential of the sample was then measured as done in the calibrations. If the concentration is greater than $2 \times 10^{-6}M F^{-}$, the result is calculated using the least squares equation for the system. If the concentration is less than $2 \times 10^{-6}M F^{-}$, the result is measured using the graph.

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