

Regulatory

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**KERR-McGEE CORPORATION**

KERR-McGEE BUILDING • OKLAHOMA CITY, OKLAHOMA 73102

May 14, 1973



Mr. J. E. Rothfleisch  
Materials Branch  
Directorate of Licensing  
U. S. Atomic Energy Commission  
Washington, D. C. 20545

Dear Mr. Rothfleisch:

Please refer to the telephone conversation wherein you requested certain additional information on raw and treated raffinate. As I stated, the analysis of fresh raffinate will vary relatively widely by the particular blend of feeds being treated since it can be expected that the degree of uranium extraction will vary by the presence of insoluble uranium occluding materials such as quartz or shales and the presence of possible complexing agents. Thorium quantities will vary widely by the source of the concentrate since Canadian materials contain significantly higher levels of thorium.

I understand that you requested from Mr. Craig heavy metal analysis of treated raffinate which is given below:

Treatment Date	4/11/73
Arsenic - mg/l	.3
Mercury - ug/l	<1
Lead - mg/l	<.2

Please let me know if you need additional information.

Sincerely,

*W. J. Shelley*  
W. J. Shelley, Director  
Regulation and Control  
Nuclear Division

WJS:srj



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# FRESH RAFFINATE ANALYSIS

<u>Date</u>	<u>Alpha</u> <u><math>\mu\text{Ci/ml} \times 10^{-6}</math></u>	<u>Beta</u> <u><math>\mu\text{Ci/ml}</math></u>	<u>Thorium</u> <u><math>\mu\text{Ci/ml} \times 10^{-8}</math></u>	<u>Radium</u> <u><math>\mu\text{Ci/ml} \times 10^{-8}</math></u>	<u>Uranium</u> <u>grams/liter</u>
7/20/71	872	640	88,500	173	.0842
11/6/72	770	14	4,580	1,460	.0056
11/6/72	870	14	2,800	1,300	.0055
October Composite	590	6	1,890	250	.0590

BOOKET NO. 40-8027

Rec'd w/lt. dtd.

MAY 14 1973

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DOCKET NO. 40-8027



KERR-McGEE CORPORATION

KERR-McGEE BUILDING • OKLAHOMA CITY, OKLAHOMA 73102

July 16, 1973

REGULATORY DOCKET FILE COPY



Mr. J. E. Rothfleisch  
Materials Branch  
Directorate of Licensing  
U.S. Atomic Energy Commission  
Washington, D.C. 20545

Dear Jack:

Please refer to your request to the plant for fluoride in air and vegetation data in 1973. I am assuming that the attached sheet is exactly what you requested, but have no way of knowing for sure. I have also included the revised analytical procedure for the determination of fluoride in air and stack gas samples which is referred to at the bottom of Chuck's submission as the apparent reason for the reduced levels measured.

I am including a revised copy of drawing 201-M-5001, Revision 2, which has revised total release number. As we have requested previously, we consider this information proprietary and request that you hold the same in accordance with provision of 10 CFR 2.790 (b). I have not gone over this in detail but continue to be concerned about its degree of accuracy. Will check it further and call you next week.

Sincerely,

W. J. Shelley, Director  
Regulation and Control  
Nuclear Division

WJS:ml

encl 3



5965

SEQUOYAH FACILITY  
FLUORIDE CONCENTRATIONS (AIR AND VEGETATION)

1972	1,000 ft. East of Facility		1,000 Ft North of Facility		1,000 Ft. South of Facility		1,000 Ft West of Facility	
	<u>Veg.</u>	<u>Air</u>	<u>Veg.</u>	<u>Air</u>	<u>Veg.</u>	<u>Air</u>	<u>Veg.</u>	<u>Air</u>
Apr		<.001		<.001		.014		<.001
May		.002		.001		.002		.002
Jun		.008		.007		.018		.005
Jul		<.001		<.001		<.001		<.001
Aug		<.001		<.001		<.001		<.001
Sep		<.001		<.001		<.001		.003
Oct		<.001		<.001		<.001		<.001
Nov	47.7	.002	18.6	<.002	16.3	<.002	41.3	<.002
Dec	41.0	.001	6.0	.009	10.6	<.002	73.0	.002
<u>1973</u>								
*Jan	14	.00032	<4	.00005	<4	.00008	31	.0016
Feb	<10	.00015	<10	.00008	<10	.00016	<10	.00026
Mar	<4	.0002	<4	.00005	<4	.00006	12	.0006
Apr	<3	.00003	<3	.00002	<3	.00003	<3	.00034
May	11	.00008	<2	.0001	<2	.0005	3	.00015

\*Air sampling for fluoride was changed from the scrubber method to Sodium Formate impregnated filter paper. This resulted in obtaining a much lower detection level.

Fluoride Air Results - Concentration in  $\mu\text{gm/liter}$ .

Fluoride Vegetation Results - Concentration in  $\mu\text{gm/gm}$ .

6/27/73  
0002

# Determination of Fluoride in Air and Stack Gas Samples by Use of an Ion Specific Electrode

Lawrence A. Eilers and Clifford E. Decker

National Center for Air Pollution Control, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio 45237

An analytical procedure for the determination of water-soluble fluoride in air and stack gas samples using a specific-ion electrode is described. Gaseous and particulate fluoride in ambient air are collected by filtration and chemisorption on membrane filters impregnated with sodium formate. Data pertaining to the collection efficiency and the dissolution of collected fluorides from ambient air samples are presented. As little as 0.25 part per billion fluoride in air can be measured with this procedure. Gaseous fluorides in stack gas are collected by reaction with a hot glass probe to form gaseous silicon tetrafluoride, which hydrolyzes in water to form soluble fluosilicic acid. Results obtained with the electrode and the Spadns-Zirconium Lake Method for fluoride in stack gas were compared, and at the 0.05 significance level, no difference existed in the two methods. This relatively new analytical tool, as applied to the analysis of air pollutants, has been shown to be rapid and convenient, and appears to be less susceptible to interferences than other methods presently available for the measurement of fluoride.

CONSIDERABLE INTEREST has been directed toward the determination of gaseous and particulate fluoride in ambient air and stack effluents. Fluoride, which has been shown to be detrimental to vegetation (1) and animals (2), is emitted into the environment from various industrial processes, such as phosphate fertilizer production, aluminum reduction, and metal smelting processes. Analytical methods for the determination of fluoride, such as volumetric (3), conductimetric (4), potentiometric (5), complexometric (6), gravimetric (7), and colorimetric (7), have been reported. The most widely accepted analytical methods for the determination of fluoride are colorimetric. These procedures require distillation of the fluoride from perchloric or sulfuric acid to remove interferences prior to the analysis (8, 9). If perchloric acid is used, the organic matter present in the sample should be destroyed before the distillation by high-temperature fusion. In addition to being time-consuming, the impurity of the reagents used for the fusion and distillation techniques add significantly to the reagent blank. Thus, the accuracy of such a method can be severely hindered if the magnitude of the reagent blank approaches that of the desired constituent. For these reasons, the existing methods are less than desirable.

In recent years, the development of specific ion electrodes has stimulated growth in the field of analytical potentiometry. An Orion specific ion electrode was used in this investigation. It consists of a fluoride-sensitive crystal of lanthanum-fluoride ( $\text{LaF}_3$ ), doped with a rare earth, europium(II), and cemented to a plastic tube containing an internal solution of 0.1M NaCl and 0.1M NaF. When the electrode is immersed in a solution of fluoride, a potential difference is established; the magnitude of the potential depends on the ratio of the fluoride ion activities between the sample and the internal solution. The potential of the electrode is measured against a saturated calomel reference electrode on an expanded-scale pH meter. The fluoride-specific-ion electrode has made possible the development of new methods for the collection and analysis of atmospheric fluoride.

Until now, two basic procedures for the collection of atmospheric fluoride were employed; namely, bubblers or impingers containing dilute alkaline solutions, and glass fiber filters using a high-volume sampler. Impingers offer a low sampling rate, a long sampling interval, poor collection efficiency for particulate fluoride, evaporation losses, and freezing of solutions; and glass fiber filters have extremely high fluoride backgrounds. The need for a simplified collection procedure for atmospheric fluoride was apparent.

Lodge, Pate, and Huitt (10) have demonstrated that remarkably long contact time is achieved when a molecule of a gas is passed through a membrane filter. Based on this information, membrane filters were chosen as the collection substrate. These filters, when impregnated with sodium formate, utilize both chemisorption and filtration for the quantitative collection of both gaseous and particulate fluorides.

To collect particulate and water-soluble gaseous fluorides from stack gases, a combination particulate and gas sampling train, as described by Smith (11), was employed. This consists of a heated glass probe, a cyclone, a Whatman No. 41 filter, and several Greenburg-Smith impingers. Gaseous fluorides in the stack gas react with the hot glass probe forming soluble fluosilicic acid and are collected in the first two Greenburg-Smith impingers. Particulate fluorides are collected in the cyclone and on the filter.

## EXPERIMENTAL

**Apparatus.** A Corning Model 12 expanded-scale pH meter was used to measure the potential difference between the Orion Model 94-99 fluoride activity electrode and a non-ferrous saturated KCl reference electrode. Details pertaining to the design and operational parameters are described by Lingane (12). A specially designed high-volume sequential sampler was built for the collection of atmospheric fluorides.

- (1) W. H. McIntire, I. J. Hardin, and Mary H. Buehler, Bulletin 279, University of Tennessee, 1958.
- (2) G. M. Merriman and C. S. Hobbs, Bulletin 347, University of Tennessee, 1962.
- (3) W. F. Hillebrand, G. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," 2nd ed., Wiley, New York, 1963, pp 742-6.
- (4) H. Kubota and J. G. Surak, *Anal. Chem.*, **31**, 283-6 (1959).
- (5) T. A. O'Donnell and D. F. Stewart, *Anal.*, **33**, 337-41 (1961).
- (6) M. A. Leonard, *Analyst*, **83**, 304-6 (1963).
- (7) E. Bellock and P. J. Schaeffer, *Anal. Chem.*, **30**, 2032-4 (1958).
- (8) E. Bellock, *J. Am. Water Works Ass.*, **56**, 530-6 (1963).
- (9) H. H. Willard and O. B. Winter, *Ind. Eng. Chem.*, **5**, 7-10 (1933).

- (10) J. P. Lodge, J. B. Pate, and H. A. Huitt, *J. Ind. Hyg.*, July-August, 330-7 (1953).
- (11) W. S. Smith and Associates, 60th Annual Meeting, APCA, Cleveland, Ohio, 1967.
- (12) J. J. Lingane, *ANAL. CHEM.*, **39**, 281-7 (1967).

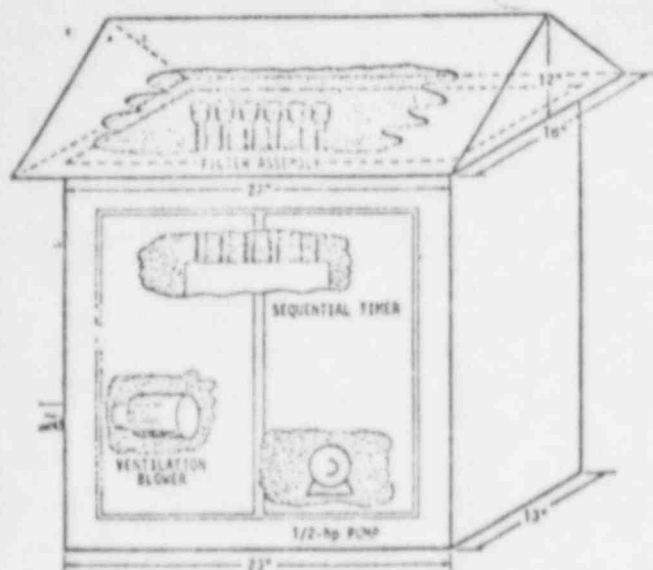


Figure 1. High-volume sequential air sampler

Construction details of this sampler are presented in Figures 1 and 2.

The fluoride collection media used in the high-volume sequential sampler consisted of membrane filters impregnated with sodium formate. These filters are prepared by immersing an 8- by 10-inch, 5-micron-pore-diameter, cellulose acetate filter sheet in a 50% ethyl alcohol solution containing 10% sodium formate. These sheets were air dried at room temperature. Filter disks, 47 mm in diameter, were cut from these sheets using an arch punch.

**Reagents.** ACS-grade chemicals were used without further purification for the preparation of all reagents. A stock solution of fluoride (10 mg/ml) was prepared by dissolving 22.105 grams of NaF in distilled water and diluting to 1 liter. Dilute fluoride standard solutions (0.1, 1, 10, 100, 1000 mg F<sup>-</sup>/liter) buffered to pH 7.5 with 0.1M sodium citrate were prepared from the stock solution by appropriate dilutions.

**Procedure.** **AMBIENT AIR SAMPLES.** Atmospheric samples are collected on the impregnated filters by sampling with the high-volume sequential sampler at an air flow rate of 4 cubic feet per minute for 4 hours. The exposed filter is inserted into a 25-ml plastic vial, and 20.0 ml of 0.1M sodium citrate is added. The vial is then placed on a reciprocal shaker for 1 hour to solubilize the fluoride present on the filter. The sample solution is transferred to a 50-ml polyethylene beaker, and the fluoride potential is measured by the specific ion electrode on an expanded-scale pH meter. The fluoride content of the sample is obtained from a calibration curve. This calibration curve is obtained by plotting the millivolt readings, as read on the expanded-scale pH meter, vs. the fluoride ion concentration of the standard solutions.

**STACK GAS SAMPLES.** Water-soluble gaseous fluorides are collected from stack effluents by means of the sampling train previously mentioned (7). A 10-ml aliquot of the composite sample from the two Greenburg-Smith impingers is added to 10 ml of 0.2M sodium citrate buffer. The fluoride content is determined, as previously described under ambient air samples.

## RESULTS AND DISCUSSION

**Determination of Collection Efficiency.** In order to determine collection efficiency of the impregnated filters, a known source of hydrogen fluoride was needed. For this purpose, HF permeation tubes were employed.

Figure 3 is a schematic diagram of a hydrogen fluoride permeation tube, which was constructed of 1/4-inch FEP Teflon (Du Pont) tubing. A Teflon plug was inserted in one end of

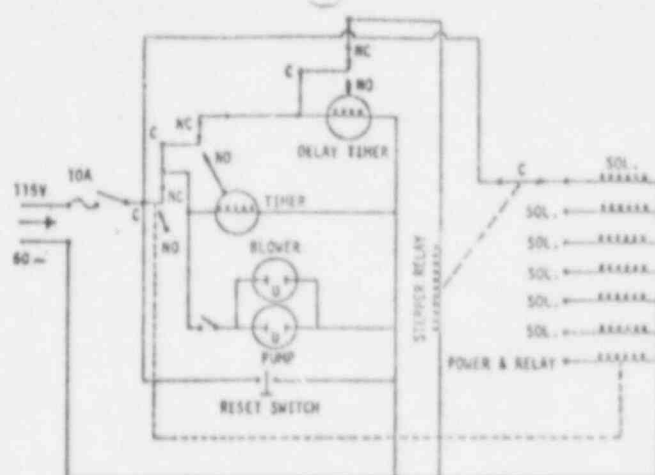


Figure 2. Schematic diagram of sequential sampler  
Materials list:

Description	No. required
Blower—15 cfm	1
Pump—Gast, 1/2-h.p. carbon valve	1
Solenoid valve 1/4-inch orifice, 115 V	6
Timer—cm—10	1
Timer rack, B 12	1
Stepper relay—M.E.R., (115 V)	1
Delay timer, 90-65 (115 V)	1
Power relay—PR 5 AY (115 V)	1

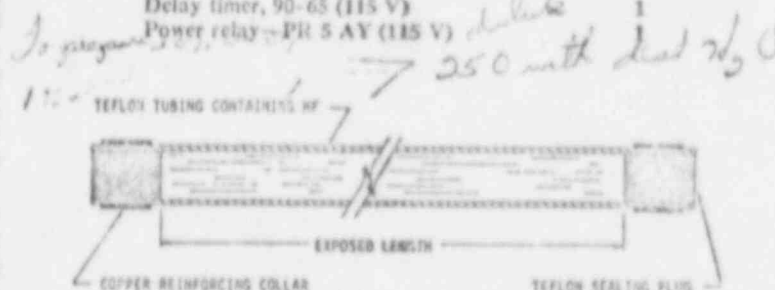


Figure 3. Hydrogen fluoride permeation tube

the tube and secured by means of a copper reinforcing collar, which was crimped in place with a flanging tool. The plugged end of the tube was immersed in a dry ice-acetone bath. Gaseous hydrogen fluoride was permitted to enter the exposed end through a capillary tube and was allowed to condense on the inside walls of the tube. When the tube was three quarters full of liquid hydrogen fluoride, the sealing plug was inserted and secured with another copper reinforcing collar (13).

The permeation tube was placed inside a Teflon tube holder and immersed in a constant temperature water bath. Diluent air was then passed through a temperature conditioning column, over the permeation tube, and out a Teflon exit tube.

Three hydrogen fluoride permeation tubes were calibrated gravimetrically to determine their permeation rate. The average hydrogen fluoride permeation rate in  $\mu\text{g HF/cm/min}$  was plotted vs. temperature on a semilog paper (Figure 4). The average standard deviation of permeation rate was found to be 0.02  $\mu\text{g HF/cm/min}$ . By varying parameters such as temperature, tube length, and diluent air flow, one can achieve almost any desired concentration of hydrogen fluoride gas.

Known concentrations of hydrogen fluoride gas from the permeation tube were drawn through two filters in series at a rate of 4 cubic feet per minute. The amount of HF collected on the filters was determined by the Spinks-Zirconium Lake Method (7).

(13) A. E. O'Keefe, National Center for Air Pollution Control, Cincinnati, Ohio, private communications, 1967.



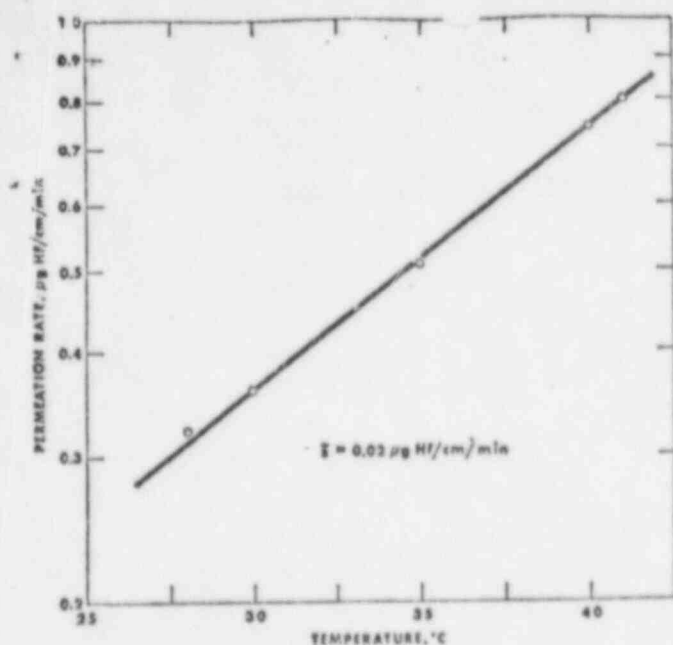


Figure 4. Calibration curve of hydrogen fluoride permeation rate vs. temperature

Fifteen determinations were made where 28  $\mu\text{g}$  of fluoride was permitted to enter two impregnated filters in series. Data from Table I demonstrate that the amount of hydrogen fluoride collected by the first filter was statistically equivalent to the amount introduced. In no case was any fluoride detected on the second filter. From these data, the collection efficiency for gaseous fluorides was determined to be quantitative. The collection efficiency for particulate fluorides was assumed to be quantitative because of the physical properties that exist while sampling through this type media (14).

Six determinations were made on unimpregnated filters using the same system as before. A collection efficiency of 30.5% was observed for these filters. The maximum quantity of HF that theoretically could react with the impregnated filter was calculated to be 17 mg, based on the average weight of sodium formate contained in the exposed area of the filter disk.

**Instrument Precision and Accuracy.** Five standards of known fluoride concentration were prepared in 0.1M sodium citrate. Analyses were performed daily on these solutions as unknowns for 6 days. From Table II, it can be seen that the largest per cent standard deviation for any measurement

(14) Technical Specifications Manual, Gelman Instrument Co., 1967.

Table I. Determination of Collection Efficiency

No. of determinations	Fluoride sampled, $\mu\text{g}$	Fluorides Recovered, $\mu\text{g}$		% Recovery (Filter 1)
		Filter 1*	Filter 2*	
15 <sup>b</sup>	28.0	28.06 $\pm$ 0.33	N.D. <sup>c</sup>	100.2 $\pm$ 1.2
6 <sup>d</sup>	63.9	19.5 $\pm$ 0.30	15.0 $\pm$ 1.0	30.5 $\pm$ 1.0

\* 5-micron pore diameter, cellulose acetate filter.

<sup>b</sup> Filters impregnated with sodium formate.

<sup>c</sup> Not detectable.

<sup>d</sup> Unimpregnated filters.

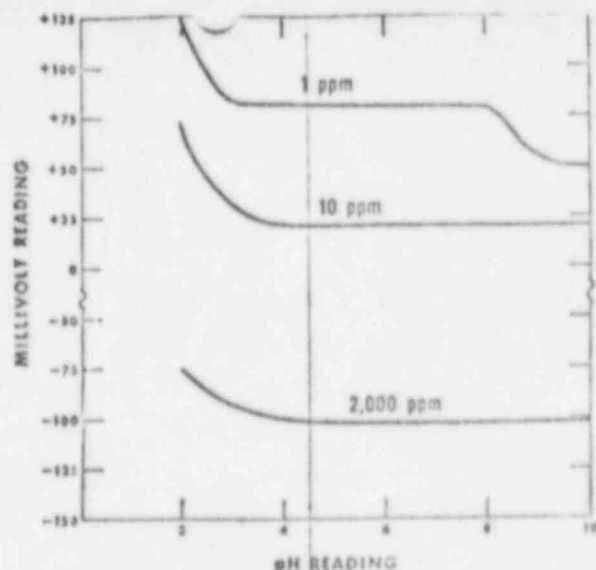


Figure 5. Effect of pH on electrode response sodium fluoride standards

was less than 5% and in most cases less than 2%. The average error incurred was in all cases less than 4%.

**Interference.** The only common interfering ions are the hydroxide ions when in excess of the fluoride concentration (15), and cations such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , which could complex the fluoride and reduce its activity.

The effect of pH on electrode response was determined at fluoride concentrations of 1, 10, and 2000 ppm. The pH of the solutions was adjusted from 2 to 10, and the electrode response measured. From Figure 5, it can be seen that electrode response was affected very little as the pH was adjusted from 5 to 8. Aluminum and iron, which are present in most atmospheric samples, are prevented from complexing the fluoride by the addition of a sodium citrate buffer, which complexes these metals, maintains a constant pH of 7.5, and controls the total ionic strength of the solution. Atmospheric samples analyzed using the electrode and the sampling procedure as previously described usually contain less than 5 ppm fluoride. For this concentration and for several orders of magnitude higher, the fluoride contribution does not appreciably change or alter the total ionic strength. Since the pH and total ionic strength are relatively constant in the samples and in the standard solution used to prepare the calibration curve, no correction for the fluoride activity is necessary.

**Analysis of Atmospheric Samples.** Method comparisons for ambient air samples proved to be impractical because of inherent high backgrounds encountered during the separation of fluorides from interferences.

In order to validate the use of the electrode for analysis of atmospheric samples, it was necessary to determine the extent to which the fluoride collected on the filter is soluble in the aqueous buffer solution. Twenty-four 4-hour atmospheric samples were collected using the impregnated filter and previously described sampler. The fluoride on these filters was subjected to dissolution by shaking in 20 ml of 0.1M sodium citrate buffer for 1 hour. The sample was then divided into two fractions by filtration. The fluoride contained in the water-soluble fraction was determined by use of the specific ion electrode. The water-insoluble fraction was subjected to

(15) M. S. Frant and J. W. Ross, Jr., *Science*, 154, 1553 (1966).

Table II. Analysis of NaF Standards for Fluoride

Fluoride concentration, ppm	Fluoride found, ppm						Error, %	
	1	2	3	4	5	6		Average*
1.7	1.67	1.80	1.80	1.80	1.75	1.68	1.75 ± 0.06	2.9
4.0	3.9	4.0	4.15	4.05	4.0	4.0	4.01 ± 0.03	0.29
20.0	20.7	20.0	20.5	20.0	20.0	20.0	20.1 ± 0.3	0.5
95.0	95.5	96.0	95.0	96.0	95.0	93.0	95.1 ± 1.1	0.1
110.0	118.0	118.0	115.0	110.0	113.0	108.0	113.7 ± 4.1	3.4

\* Error expressed as one standard deviation.

perchloric acid distillation without prior fusion to separate any fluoride from the insoluble material and analyzed by the Spadns-Zirconium Lake Method. The average water-soluble fluoride for these samples was 18.4  $\mu\text{g}$ . The water-insoluble fraction amounted to 5.4  $\mu\text{g}$ , which was equivalent to the distillation-reagent blank. These data substantiate that the atmospheric fluoride as collected on this substrate was essentially water-soluble; and, therefore, would be available for measurement by the specific-ion electrode. In general, the solubility of the commonly encountered fluoride compounds in ambient air is of a sufficient magnitude for their complete dissolution in the 20-ml volume of solvent employed in the method. For example, over 300  $\mu\text{g}$  of  $\text{CaF}_2$  would be soluble under these conditions.

**Analysis of Stack Gas Samples.** Over 50 gaseous samples collected from phosphate fertilizer plant effluents were analyzed by the previously described procedure and the Spadns-Zirconium Lake Method.

The results of these analyses were divided into two concentration ranges for statistical analysis. Using the paired "t" test at the 0.05 significance level, there was no basis for saying that the results with the electrode method differed from results of the Spadns Method.

#### SUMMARY

This method, designed for the collection of gaseous and particulate fluoride at ambient levels of 1  $\mu\text{g}/\text{m}^3$  or less, avoids the difficulties encountered with bubblers or glass fiber filters,

and provides a means of sampling large volumes of air in a relatively short period of time. Cellulose acetate membrane filters impregnated with sodium formate have been shown to be quantitative for the collection of atmospheric fluoride. The utilization of these filters and the specially designed high-volume sampler as the collection device, followed by analysis of the solubilized fluoride using the Orion specific-ion electrode, permits fluoride determinations to as little as 0.25 ppb in ambient air. Analyses of stack gas samples have been made by this method and the Spadns-Zirconium Lake Method, and the results of these methods were shown to be statistically equivalent. Approximately 100 samples have been analyzed by this method in an 8-hour period. The use of the fluoride specific-ion electrode has been shown to be more rapid, convenient, and appears to be less susceptible to interferences than existing methods for determining microgram quantities of fluoride.

#### ACKNOWLEDGMENT

The authors express their appreciation to Seymour Hochheiser for his helpful suggestions and advice throughout this work.

RECEIVED for review May 8, 1968. Accepted June 13, 1968. Presented at the 154th National Meeting, ACS, Chicago, Ill., September 1967. Reference to specific brands is made for identification only and does not imply endorsement by the Public Health Service.

## Corrections

### Analytical Study of a Sulfide Ion-Selective Membrane Electrode in Alkaline Solution

In this article by T. M. Hsu and G. A. Rechnitz [ANAL. CHEM., 40, 1054 (1968)] explicit reference to the instruction manual for the Orion 94-61 electrode was omitted on pages 1055 and 1056. On page 1054, an earlier relevant study by Ross and Frant entitled "A New Electrode for Sulfide Ion Activity," which was presented at the 1966 Eastern Analytical Symposium, should have been incorporated as a reference.

### Correlation between Molecular Structure of Sterols and Retention Time in Gas Chromatography

In this article by Nobuo Ikekawa *et al.* [ANAL. CHEM., 40, 1139 (1968)] two errors appear in Table I (page 1140). First, all of the figures in column 7 (headed XE-60) should be 2.3 times as much as the values appearing in the table. The corrected values are as follows: 4.74, 4.32, 4.78, 5.47, 4.55, 4.74, 4.37, 5.80, 4.99; 5.98, 5.98, 5.84, 7.66, 5.17, 7.31, 6.37, 5.91, 6.28; 7.56, 7.65, 8.32, 9.56, 6.32, 7.91, 7.61, 7.68, 7.61, 8.80, 7.56. Second, in the footnote for Table I, the figure in column 4, line 5, should be 4.0 minutes instead of 9.2 minutes.