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The determination of fluoride in silicate rocks by ion-selective electrode: an update

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ABSTRACT

This report discusses the details from an updating of the sodium carbonate/zinc oxide fusion ion-selective electrode procedure (Ingram, 1970) for the determination of fluoride in silicate rocks. In the revised method the sample (-100 mesh) is fused with a mixture of sodium carbonate and zinc oxide, leached with distilled water, centrifuged, and the solution is decanted into a disposable polypropylene beaker. The residue is discarded. Carbon dioxide is expelled from the solution by the addition of hydrochloric acid, and the solution is diluted to a fixed weight with distilled water. An aliquot of this solution is further diluted with an aliquot of sodium citrate-potassium nitrate buffer solution. The fluoride concentration then is determined by measurement of the potential produced by a fluoride ion-selective electrode. These modifications double sample output with a determination limit of about 50 ppm fluoride, and a relative standard deviation of less than ten percent.

INTRODUCTION

The procedure (Ingram, 1970) works well for the determination of fluoride in silicate rocks. The concentration of citrate in the sodium citrate-potassium nitrate buffer is very effective in controlling aluminum interference. The buffer also controls the pH of the sample and standard solutions. The pH of the buffered solutions normally falls in the range of 6.3-6.8 which is acceptable for the determination of fluoride by ion-selective electrode. In order to increase the number of samples analyzed and also to make the analytical work less tedious, the Ingram procedure has been modified and streamlined. Inexpensive, disposable polypropylene labware is used throughout to avoid cleaning five pieces of glassware per sample. Centrifuging replaces filtering for removing the insoluble carbonate residue. These modifications increase sample output from an average of 7.5 to about 15 samples per workday.

APPARATUS

1. Measurements are made with an Orion Research Expandable Ion Analyzer (model EA920), equipped with a combination fluoride electrode (model 96-09).

2. Corning polypropylene 50-mL, sterile, graduated centrifuge tubes with screw caps.

3. Graduated 4-oz non-sterile polypropylene sample containers with polyethylene caps, available from the Cole-Parmer Instrument Company, Chicago, IL.

4. Platinum crucibles (10 mL) with covers.

REAGENTS

1. Hydrochloric acid: 6M.

2. 0.2M sodium citrate-0.2M potassium nitrate solution: Dissolve 59 grams of sodium citrate dihydrate and 20 grams of potassium nitrate in distilled water and dilute to 1 liter.

3. Sodium fluoride standard: Purify the sodium fluoride by first adding 10 to 15 mL of concentrated hydrofluoric acid to 3 grams of sodium fluoride in a platinum dish. Evaporate the resulting solution to dryness on a steam bath. Transfer the purified sodium fluoride to a polyethylene vial.

4. Standard A: Prepare a "stock" solution of 1000 µg/mL fluoride in distilled water by first dissolving 1.105 g of the purified sodium fluoride and by then diluting the resulting solution to 500 mL.

5. Standard B: Prepare a 100 µg/mL fluoride standard by diluting 10.0 mL of standard A to 100 mL.

6. Standard C: Prepare a 10 µg/mL fluoride standard by diluting 1.0 mL of standard A to 100 mL.

7. Calibration standards: Add 0.5 g of anhydrous sodium carbonate to each of ten tared 4-oz polypropylene sample containers and then add about 50 mL distilled water to dissolve the sodium carbonate. Add 2 mL of 6M hydrochloric acid; swirl container to expel all the carbon dioxide; add the appropriate amount of standard B or standard C (Table 1) and adjust to 100.4 g with distilled water. Close container with the polyethylene cap. Later in the procedure when these calibration standards are mixed 1:1 with 0.2M sodium citrate-0.2M potassium nitrate buffer, the fluoride concentration is diluted to half the value given in Table 1.

TABLE 1.--Dilutions for Preparation of Individual Calibration Standards

Pipet volume (mL)	Standard pipeted (B or C)	Adjust to final weight (g)	Final concentration of fluoride (µg/mL)
0.2	C	100.4	.02
0.5	C	100.4	.05
1.0	C	100.4	.10
1.5	C	100.4	.15
2.0	C	100.4	.20
3.0	C	100.4	.30
4.0	C	100.4	.40
8.0	C	100.4	.80
1.0	B	100.4	1.0
2.0	B	100.4	2.0

PROCEDURE

1. Thoroughly clean each 10-mL platinum crucible by first fusing with sodium carbonate and then by washing the crucible in dilute (1+1) hdyrochloric acid and rinsing in distilled water. This step is necessary to avoid contamination.

2. Weigh 0.100 g of ground (-100 mesh) silicate rock, and transfer to a 10-mL platinum crucible.

3. Add 0.5 g of anhydrous sodium carbonate and 0.1 g zinc oxide to the crucible and mix thoroughly with a thin glass stirring rod. Zinc oxide aids in the decomposition of refractory fluorides. It also aids in leaching out fluorides from silica since the zinc silicate, formed in the decomposition, has a relatively low absorption activity and fluoride is not absorbed on its surface (Dolezal et al., 1968, p. 171).

4. Place in an electric furnace at 1000^{o}C and fuse for 30 min.

5. Allow crucible to cool and place it on a low-temperature hot plate or on top of a steam bath. Fill crucible with distilled water, cover, and warm at 50°C to 90°C overnight to leach the fused mass.

6. Quantitatively transfer the contents of the crucible to a graduated polypropylene 50-mL centrifuge tube. Break up any lumps with a Teflon stirring rod and add distilled water to the 45-mL mark. Close the tube with a screw cap and mix by inverting tube.

7. Centrifuge at 2000 RPM for 10 min.

8. Decant solution into a tared, graduated 4-oz polypropylene sample container. Add 2 mL of 6M hydrochloric acid and swirl container to expel all the carbon dioxide. Place container on an open analytical balance and weigh to 100.4 g with distilled water. Close the container with a polyethylene cap.

9. Measurements of electrode potentials may be accomplished according to Ingram (1970) in which the calibration standards and samples are mixed 1:1 with 0.2M sodium citrate-0.2M potassium nitrate buffer solution. However, by using the computerized "ready" signal of the Orion Ion Analyzer (model EA920) and the combination fluoride-ion electrode (model 96-09), it is not necessary to equilibrate the electrode after each sample and standard. Samples and standards having a fluoride concentration above 0.1 ppm in solution normally come to equilibrium in 5 min. Samples containing less than 0.1 ppm in solution may take 5 to 10 min before reaching equilibrium for an accurate measurement.

CALCULATIONS

Upon completion of all measurements of electrode potentials for samples and calibration standards, graphically establish a functional relationship between concentration and electrode potential by plotting fluoride concentration, µg/mL, versus potential, mV. The relationship generally is plotted on one-cycle semi-logarithmic paper. For a sample weighing 0.100 g, the concentration of fluoride in the sample, in units of ug/g, equals 2000 times the concentration of fluoride in solution, µg/mL, as obtained from the calibration curve.

ACCURACY, PRECISION, AND DETECTABILITY

Table 2. Fluoride Values and Standard Deviations of Reference Samples

Reference Sample	Fluoride, average values (ppm)	Standard deviation	Percent RSD	Number of determinations	Fluoride, reported values (ppm)
USGS W-1	223	17.7	7.9	21	250(a); 240(b); 235(f)
USGS BHVO-1	360	17.0	4.7	10	380(c); 397(e); 390(f)
USGS G-2	1290	44.6	3.5	14	1290(a); 1480(b); 1295(f)
USGS AGV-1	453	9.6	2.1	4	435(a); 435(f)
USGS BCR-1	458	17.8	3.9	11	470(a); 490(f)
USGS GSP-1	3500	All replicates are 3500 ppm		4	3200(a); 3870,3856(b); 3600(f)
USGS RGM-1	356	17.2	4.8	7	325(c); 342(d); 383(e); 345(f)
CCRMP MRG-1	234	--	--	1	250(g)+

CCRMP: Canadian Certified Reference Materials Project

(a) Flanagan, 1976.

(b) Ingram, 1970.

(c) Troll and Farzaneh, 1980.

(d) Machacek et al., 1976.

(e) Fuge, 1981.

(f) Stecher, 1983.

(g) Abbey, 1983.

+ Fluoride content reported as 0.025 percent on a dry basis.

DISCUSSION AND CONCLUSIONS

The pH of the fluoride solution to be measured with the ion-specific electrode is critical. At a pH below 5.5, the measurement gives concentrations that are biased low because of F^- complexing with H^+. A high bias in the measured concentration occurs at pH values above 7.0 because of the presence of high concentrations of OH^- or HCO_3^-. The pH of the solutions buffered with sodium citrate-potassium nitrate falls in the optimum range of 6.3-6.8. According to Ingram (1970) samples containing 28 percent Al_2O_3 and 0.004 to 0.08 percent fluoride can be analyzed without aluminum interference and if more than 0.08 percent fluoride is present, at least 38 percent Al_2O_3 can be present. This is well within the Al_2O_3 concentration found in silicates. The lower limit of determination by the ion-selective method for fluoride is based on the variation in the fluoride blank and in the sensitivity of the electrode. For a 0.100-g sample, the lower limit of determination may range from 0.004 percent to 0.01 percent. Fluoride analyses obtained over the years in this laboratory have resulted in a relative standard deviation (RSD) of about 10 percent using the Ingram procedure, and it would take 4 workdays to complete 30 samples. With the modifications mentioned in this report, not only has the RSD of the fluoride determination improved (Table 2), but 45 samples can be completed in 3 workdays.

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