

REPORT NO. 1886

**A RAPID METHOD FOR THE DETERMINATION OF
FLUORIDE IN GEOLOGICAL SAMPLES**

Director of Division T.W. Steele

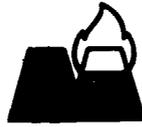
Investigators M. Josephson
E.B.T. Cook
K. Dixon

Date 31st March, 1977

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**NATIONAL
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SYNOPSIS

An account is given of a rapid procedure for the determination by use of the specific-ion electrode of fluoride in geological samples.

The sample is fused with sodium hydroxide in a nickel crucible in a muffle furnace. The melt is leached with water, a buffer solution of ammonium citrate is added, and the fluoride activity is measured with a specific-ion electrode.

All operations are carried out in the crucible, making possible approximately 100 determinations a day. The precision of the method is approximately 10 per cent at a fluoride concentration of 500 p.p.m., which is acceptable for geological-survey work.

SAMEVATTING

Daar word verslag gedoen oor 'n vinnige prosedure vir die bepaling van fluoriëd in geologiese monsters met gebruik van die spesifieke-ioonelektrode.

Die monster word met natriumhidroksied in 'n nikkelkroesie in 'n moffeloond gesmelt. Die smeltel word met water uitgeloo, 'n bufferoplossing van ammoniumsitraat bygevoeg en die fluoriëdaktiwiteit met 'n spesifieke-ioonelektrode gemeet.

Alle bewerkings word in die kroesie uitgevoer sodat daar ongeveer 100 bepalinge per dag gedoen kan word. Die presisie van die metode is ongeveer 10 persent met 'n fluoriëdkonsentrasie van 500 d.p.m. wat aanvaarbaar is vir geologiese-opnamewerk.

CONTENTS

1. INTRODUCTION	1
2. EXPERIMENTAL METHOD	1
2.1. ELIMINATION OF OPERATING STEPS	1
2.1.1. Addition of Citrate	1
2.1.2. Fusion with Sodium Hydroxide	1
2.1.3. Tolerance of Buffer to Aluminium	2
2.2. CALIBRATION	2
3. RESULTS	3
3.1. PRECISION OF MEASUREMENT	3
3.2. ACCURACY OF METHOD	4
4. DISCUSSION	4
5. CONCLUSIONS	4
6. REFERENCES	4
Table 1 Effect on fluoride determination of increasing aluminium	2
Table 2 Comparison of standard solutions prepared with and without fusion	3
Table 3 Precision trials on Sample 2817 CD 78	3
Table 4 Accuracy of the method	4
Appendix A rapid method for the determination of fluoride in geological samples. (Laboratory Method No. 9/17)	6
Figure 1-1 Electrode assembly for ion-selective measurement	8

1. INTRODUCTION

A rapid method was sought for the direct determination of fluoride in geological samples without a prior separation. A throughput of approximately 100 samples per day was aimed at, and, since an accuracy of 10 to 15 per cent at a fluoride concentration of 500 p.p.m. (the lower limit) was considered acceptable, available methods that incorporate the fluoride specific-ion electrode were investigated.

A tentative method¹ incorporating the specific-ion electrode was found to be time-consuming and unsatisfactory. The method involved fusion of the sample in a furnace at 900°C with sodium carbonate and zinc oxide, extraction of the melt with hot water, and buffering with ethylenediaminetetra-acetic acid (EDTA) before measurement. Difficulty was encountered in the achievement of a clean leach of the melt, and the low fluoride concentrations (0.05 p.p.m. of fluoride in solution for a sample containing 500 p.p.m. of fluoride) were unsatisfactory for stable measurement.

An alternative method involving a specific-ion electrode, reported by Kesler *et al.*², for the analysis of fluoride in rocks and application to exploration was found to be a simpler procedure and gave satisfactory results. However, this method was not sufficiently rapid for the throughput of samples envisaged, and certain modifications were needed before it could be applied to a large number of samples.

The following modifications were considered necessary to give a more rapid method:

- (a) all operations were to be carried out *in situ* in a crucible of adequate capacity, and
- (b) the number of steps involving additions were to be reduced but the final pH value of the solution was to be maintained.

Because of the envisaged measurement *in situ*, the total volume of the solution for analysis had to be reduced (say to 35 ml if the capacity of the crucible were 50 ml), a step that could be effected only by a reduction in the amount of buffer solution used. The principal aspects requiring investigation were therefore the efficiency of the reduced volume of buffer solution, the method of calibration, and the procedure to be adopted for the measurements by ion-selective electrode in the minimum of time, 3 to 4 minutes usually being required for each measurement.

2. EXPERIMENTAL METHOD

The procedure in the method of Kesler *et al.* involves fusion, in a muffle furnace at 620°C ± 10°C for 20 minutes, of a sample of 0.1 g (less than 200 mesh) in a nickel crucible with ten pellets of sodium hydroxide. The adhering cake in the cooled crucible is then leached with water and the leach liquor is transferred to a plastic beaker. Concentrated nitric acid is added while the solution is being stirred until all the gelatinous precipitate has just dissolved, 45 g of ammonium citrate is added, and the solution is diluted to 100 ml with distilled water. Ten pellets of sodium hydroxide are added and dissolved to bring the pH value of the solution to between 5 and 7. After the fluoride activity has stabilized, millivolt readings are taken and compared with those obtained for standards in a similar matrix by the direct or standard-addition method.

2.1. Elimination of Operating Steps

2.1.1. Addition of Citrate

It was considered that, if the nitric acid were omitted, the citrate would neutralize the sodium hydroxide and act as a buffer in the solution. Thus, the addition of nitric acid and subsequently of sodium hydroxide could be omitted and the correct pH in solution could be maintained. In view of the high concentration of ammonium citrate used by Kesler *et al.*, and the need to keep the volume of citrate at a low level, this addition was reduced to 15 g in a volume of 25 ml. Difficulty was experienced in maintaining citrate in solution at higher concentrations. The pH value of the resulting solution was about 6.2, which is within the limits specified by Kesler *et al.* In the interest of speed, the citrate was added in the form of a solution from a dispenser.

2.1.2. Fusion with Sodium Hydroxide

The procedure recommended by Kesler *et al.* was to count a number of pellets of hydroxide with which to fuse the sample. Variations in acidity and pH during dissolution of the sample are of no consequence when a final adjustment of pH is made, but are important when this step is omitted and final adjustment of pH is made by the addition of ammonium citrate.

As was possibly to be expected, ten pellets of sodium hydroxide counted from one bottle had a total mass twice as great as that of ten pellets counted from another bottle and, after buffering with

DETERMINATION OF FLUORIDE

citrate, gave final pH values of 5.3 and 5.9, the lower pH value being just inside the limits given², but at a level that was subsequently shown to give low results. It was therefore necessary to adopt the slightly slower procedure of weighing the pellets on a top-loading balance.

2.1.3. Tolerance of Buffer to Aluminium

Kesler *et al.* proposed the addition of 45 g of citrate as buffer to a solution of 0.1 g of sample. It was not considered advisable to reduce the sample mass to less than 0.1 g, because even this is low for a representative sample unless the sample is very finely ground. The ratio of buffer to sample in the proposed method had therefore to be reduced by a factor of 3. No data are given by Kesler *et al.* as to the relation between aluminium and citrate and the possible interference in the determination of fluoride. If the reduced amount of citrate is sufficient to mask the highest amount of aluminium likely to be present in 0.1 g of sample the higher fluoride concentrations should lead to better stability of measurement and a reduction in memory effect from samples of variable composition.

The tolerance of aluminium to a smaller amount of buffer was assessed as follows. A reference material of basalt, BCR-1, which has an aluminium content of 7.2 per cent and an estimated fluoride content of 470 p.p.m.³, was analysed for fluoride both with and without the additional aluminium equivalent of 17 per cent in the sample. Calibration in this instance was effected by the addition of fluoride to the aqueous solution resulting from the fusion of sodium hydroxide in a nickel crucible, the same procedure being used as for the sample. The results are given in Table 1, which shows that the two values agree to within 6 per cent. These values fall in the middle of the range of values recorded by different procedures, indicating the efficiency of the amount of citrate used as a buffer.

TABLE 1

Effect on fluoride determination of increasing aluminium

Sample	Literature value (p.p.m. of F)	Kesler ² method (p.p.m. of F)	Method 9/15 ¹ (p.p.m. of F)	Proposed method (p.p.m. of F)
(Basalt) BCR-1 Std (7.2% Al)	470	545	523	492
BCR-1 (+ Al spike, = 17% in sample)				525

2.2. Calibration

Before any measurements were made, the solutions were allowed to stand so that the activity of the fluoride ion could reach a maximum in the presence of the buffer. A rate of change in the potential measured of about 1 mV per 30 seconds was considered sufficiently stable. Such a condition was generally reached after a standing period of 2 hours. A change of 1 mV corresponds to a 4 per cent error in determination.

Calibration was effected initially by the addition of fluoride to solutions containing caustic soda and ammonium citrate, and by plotting of the potential difference versus concentration on a semi-log scale to give a linear calibration with a slope of 58 mV per decade. The values obtained for the control sample under these conditions were low. At that stage it could be assumed only that the introduction of nickel from the crucible during the fusion was contributing significantly to the total ionic strength of the solutions and was affecting the calibration. Table 2 illustrates the effect of the increased total ionic strength of the solution on the determinations of 1.7 p.p.m. of fluoride ion (equivalent to 500 p.p.m. in a sample). In these tests, the additions of fluoride ions were made both before and after the fusion step. The increase in the recorded value increases very significantly.

DETERMINATION OF FLUORIDE

TABLE 2

Comparison of standard solutions prepared with and without fusion

Fluoride concn p.p.m.	Potential after fusion mV	Potential without fusion mV	Apparent F concn after fusion, p.p.m.	Apparent F concn without fusion, p.p.m.
1,7	-15,5	-21,5	2,23	1,29
1,7	-16,1	-23,2		
1,7	-13,5	-21,0		
	-16,0*			
	-16,2*			

*Fluoride added to standard solutions before fusion

The value subsequently obtained for the control sample (when it was calibrated with standard solutions carried through the whole procedure incorporating the fusion step) was 436 p.p.m. (Table 3), as compared with 414 p.p.m. obtained by Laboratory Method 9/15¹.

3. RESULTS

3.1. Precision of measurement

A coefficient of variation was determined for 12 duplicate masses of a sample that contained 400 p.p.m. of fluoride. Measurements were referred to standard fluoride solutions that had been carried through the fusion procedure as well as to solutions that had been matched with regard to salts only. In addition, the measurement of the samples was alternated with the measurement of a fluoride solution having a concentration approximately six times that of the sample. As shown in Table 3, the coefficient of variation for measurements at a constant level of fluoride ions was 10,0 per cent. For the alternating measurements, the coefficient of variation was 15,4 per cent.

TABLE 3

Precision trials on Sample 2817 CD 78

	Measurements at constant F level p.p.m.
Mean value (Std solution without fusion)	346
Mean value (Std solution with fusion)	436
Value determined by external laboratory ¹	500 to 550
Value determined by Method 9/15 ²	414
Coefficient of variation	10,0%

The coefficient of variation, even when the electrode was subjected to intermittent immersion in solutions of high fluoride concentration, was considered adequate for a rapid method for geochemical samples.

DETERMINATION OF FLUORIDE

3.2. Accuracy of Method

The comparative values for three samples are given in Table 4.

TABLE 4

Accuracy of the method

Sample	Fluoride, p.p.m.		
	Proposed method	Method 9/15 ¹	Other reported values
BCR-1	492		545 ⁽²⁾
	525	523	470 ⁽³⁾
Control sample	436	414	
B11976	2257	2351	

The agreement between the values for the sample most analysed (BCR-1) is very satisfactory. The agreement of the proposed method with Method 9/15 is good for the other two samples.

4. DISCUSSION

The modifications proposed for the method of Kesler *et al.* give rise to no serious interferences when the ratio of aluminium in the sample to that in the buffer is increased threefold. However, zirconium at a concentration of approximately 0.5 per cent forms complexes with fluoride that have a significant effect on the results. As an example, the recovery* of fluoride ion in lujavrite⁵ (zirconium concentration 1.3 per cent) was 55 per cent and 69 per cent for sample masses of 0.1 g and 0.03 g respectively.

Zirconium at these high levels is not often found in samples with high fluoride values (more than 750 p.p.m.), but its effect when encountered at concentrations greater than about 0.3 per cent should be considered if this method is used.

The proposed modification of reduction in volume makes it possible for all the operations and the measurement to be conducted in a crucible, which is a decided advantage when a rapid method is required.

Because electrode potentials developed in the same standard solution can vary by several millivolts a day, it is suggested that, when a large number of samples are measured, standards should be rechecked at regular intervals, say after every 20 samples or 20 minutes.

It is envisaged that 200 samples can be analysed over two days by one person, i.e., one day for the preparation of the samples, and the next day for the measurement. The actual procedure adopted would depend on the number of furnaces and crucibles available.

5. CONCLUSIONS

The modified procedure for the direct determination of fluoride in geological soil of samples gives satisfactory results.

The method is rapid and can be adapted to the handling of large numbers of samples. The precision and accuracy of the method are acceptable for geological-survey work.

6. REFERENCES

1. ANGLO AMERICAN RESEARCH LABORATORY. Private communication.
2. KESLER, S.E., VAN LOON, J.C., and BATESON, J.H. Analysis of fluoride in rocks and an application to exploration. *J. geochem. Explor.*, vol. 2, 1973, pp. 11-17.
3. FLANAGAN, F.J. 1972 values for international geochemical reference samples. *Geochim. cosmochim. Acta*, vol. 37, 1973, pp. 1189-1200.

*Recovery means amount determined as a percentage of the amount present.

DETERMINATION OF FLUORIDE

4. COOK, E.B.T., HOLAN, H., and STEELE, T.W. The determination, by ion-selective electrode, of fluoride in complex materials. Johannesburg, National Institute for Metallurgy, *Report no. 1781*. 5th Feb., 1976.
5. RUSSELL, B.G., *et al.* Preliminary report on the analysis of the six NIMROC geochemical samples. Johannesburg, National Institute for Metallurgy, *Report no. 1351*. 30th May, 1972.

APPENDIX

A RAPID METHOD FOR THE DETERMINATION OF FLUORIDE IN GEOLOGICAL
SAMPLES
(LABORATORY METHOD No. 9/17)

1. OUTLINE

The sample is fused with sodium hydroxide in a nickel crucible in a muffle furnace. The melt is leached with water, a buffer solution of ammonium citrate is added, and the fluoride activity is measured by a specific-ion electrode.

2. APPLICATION

The method is applicable to samples of soil and has a coefficient of variation of approximately 10 to 15 per cent. Zirconium interferes if present in concentrations of more than about 0.5 per cent.

3. APPARATUS

(1) *Electrode Assembly for Ion-selective Measurement*

See Figure 1-1, and for further details consult Reference 1.

(2) *Potentiometer*

pH-millivoltmeter graduated in divisions of 1 mV.

4. REAGENTS

(1) *Sodium Hydroxide*

A.R.-grade pellets.

(2) *Ammonium Hydroxide*

A.R. grade, sp. gr. 0.91.

(3) *Citric Acid*

Monohydrate $\text{H}_3\text{C}_6\text{H}_7\text{O}_7 \cdot \text{H}_2\text{O}$.

(4) *Di-ammonium Hydrogen Citrate Buffer Solution*

$(\text{NH}_4)_2\text{HC}_6\text{H}_7\text{O}_7$; Merck.

Weigh out 300 g of the salt in a 1-litre beaker and add 200 ml of water. Heat to near boiling while stirring until the solution clears. Allow to cool, and dilute to a volume of 500 ml. Use 25 ml of this solution for each sample. Alternatively, weigh out 279 g of citric acid monohydrate crystals in a 1-litre beaker and place it in ice-cold water. Carefully add 240 ml of concentrated ammonium hydroxide (sp. gr. 0.91) while stirring until all the acid has dissolved. Dilute to 500 ml with water. Use 25 ml of this solution for each sample.

(5) *Sodium Fluoride Stock Solution*

Take 2.2100 g of the salt dried at 150°C for 2 hours, and dissolve it in 100 ml of water in a polythene beaker. Transfer the solution to a 1-litre flask and dilute to volume with water. Store in a polythene bottle.

1 ml = 1000 μg of F.

(6) *Diluted Sodium Fluoride Solutions*

A. Dilute 35 ml of stock solution to 1 litre.

1 ml = 35.0 μg of F.

B. Dilute 250 ml of solution A to 500 ml.

1 ml = 17.5 μg of F.

C. Dilute 100 ml of solution A to 1 litre.

1 ml = 3.5 μg of F.

DETERMINATION OF FLUORIDE

5. PROCEDURE

- a. Transfer 0.1 g (± 0.003 g) of sample to a 50 ml nickel crucible.
- b. Counterpoise the crucible on a top-loading balance and add 2 g (± 0.1 g) of sodium hydroxide pellets.
- c. Place the crucible in a muffle furnace at 620°C ($\pm 10^\circ\text{C}$) for 20 minutes.
- d. Remove the crucible, and allow it to cool for 15 minutes.
- e. Add 10 ml of water from an automatic dispenser or measuring cylinder, and place the crucible on a hot-plate of moderate temperature for approximately 7 minutes. Care should be exercised to prevent violent boiling resulting from the exothermic reaction between sodium hydroxide and water.
- f. Swirl to detach adhering cake and allow to cool for about 10 minutes.
- g. Add 25 ml of ammonium citrate buffer solution from a measuring cylinder or automatic dispenser. Stir with a glass rod, cover with a watch-glass, and cool in a water-bath. The pH value of the solution should be between 5.6 and 7. Allow to stand for 2 hours, or preferably overnight.
- h. Condition the electrodes as follows. Rinse the electrode with distilled water and, after removing surplus water with a soft tissue, lower the assembly into the first sample solution. Switch the potentiometer to the appropriate scale, start the compressed-air stirrer, and, after ten minutes, record the potential. Switch to the zero position, stop the stirrer, and, after withdrawing the electrodes, remove the surplus water as before. Lower the assembly into the next sample and, after exactly one minute, record the potential. Proceed in this way for all the samples, and introduce an appropriate standard fluoride solution after every twentieth sample.

6. CALIBRATION

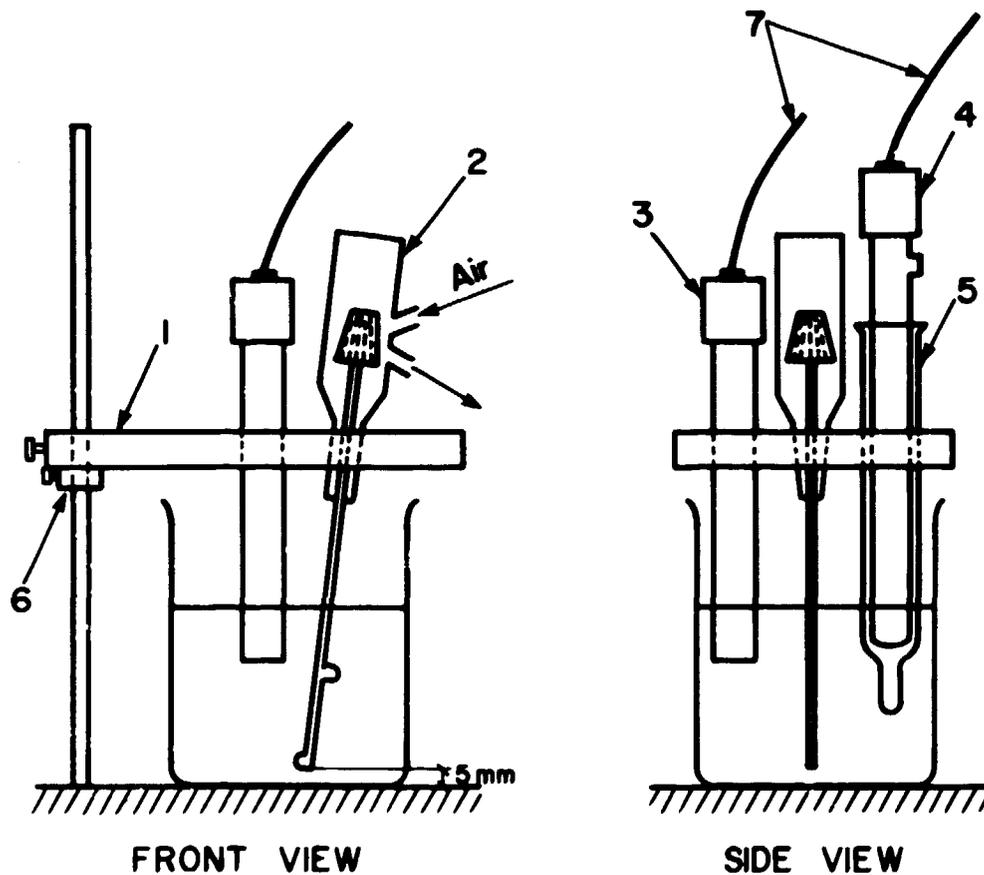
Prepare the requisite fluoride standards together with the samples as follows.

- a. To each of three nickel crucibles, add 2 g of sodium hydroxide pellets and treat as described for the samples in steps c and d of Section 5.
- b. Instead of water as described in step e of Section 5, add in sequence, by means of a pipette, 10 ml of standard fluoride solutions A, B, and C respectively to the crucibles. Proceed as described for the samples in steps e to h of Section 5. These three solutions have fluoride concentrations of 10 p.p.m., 5 p.p.m., and 1 p.p.m. respectively.
- c. Plot the millivolt readings of these standard solutions against their respective fluoride concentrations on semi-logarithmic paper in order to compute the fluoride concentration of the samples from the resulting graph. Alternatively, evaluate the fluoride concentration by entering the potential readings on a desk computer that has been suitably programmed, e.g., as previously reported by Cook *et al.*¹.

7. REFERENCE

1. COOK, E.B.T., DIXON, K., SUMMERSON, C., HOLAN, H., SHELTON, B.J., and STEEL, E. T.W. Examination of the methods of analysis for calcium fluoride in fluorspar. Johannesburg. National Institute for Metallurgy. *Report no. 1646*. 1974.

DETERMINATION OF FLUORIDE



Cell assembly

- 1 Polythene electrode holder
- 2 Compressed-air stirrer (Quickfit catalogue no.MU8/O)
- 3 Fluoride-sensitive electrode (Orion Research Model 94-09A)
- 4 Reference electrode (Ingold)
- 5 Electrolyte bridge (Ingold)
- 6 Height-adjustment collar
- 7 Electric leads to potentiometer

FIGURE I-1 Electrode assembly for ion-selective measurement