

# **DETERMINATION OF FLUORIDE IN FLUOMICA AND FLUOMICA-ALUMINA COMPOSITES WITH THE FLUORIDE ELECTRODE**

THOMAS A. FERRARO, Jr.  
POLYMER & CHEMISTRY DIVISION

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER  
Watertown, Massachusetts 02172

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## ABSTRACT

Fluoride is determined in barium fluomica and barium fluomica-alumina composites by direct potentiometric measurement with a fluoride specific-ion electrode. Measurements at pH 8 and pH 12 are compared using different methods of sample decomposition and preparation. Since the fluoride recoveries are the same in each case, direct measurement in an aqueous sodium carbonate medium is the method of choice. This method is simple and rapid since the addition of complexing and buffering agents is not required nor is the adjustment of pH necessary. (Author)

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## INTRODUCTION

Recent studies have shown that the brittleness and poor machinability of ceramic materials can be substantially improved by the addition of a second, ductile phase into the ceramic matrices. These studies have also proven that properties such as hardness and strength can be controlled and predicted by the systematic incorporation of such a second phase. The feasibility of this approach has recently been successfully demonstrated by hot pressing gamma-alumina with varying amounts of barium fluomica to fabricate composites having a wide range of controllable and predictable properties.<sup>1</sup>

In the fabrication process, parameters such as temperature and pressure must be optimized to insure full densification and thorough bonding of the mica flakes to the alumina matrix while at the same time minimizing chemical interaction between the phases. Such interaction would be evidenced by the formation of spinel at the matrix-mica interface and the volatilization of fluorides. A quantitative evaluation of the occurrence and extent of this phase degradation can thus be made by monitoring the fluoride content of the initial mica and the prepared composites. It is to this end, the establishment of a testing method applicable to the determination of fluorine in fluorine micas and fluorine mica-ceramic composites, that the work reported herein was performed.

In recent years the use of the fluoride ion-selective electrode has become widespread as a means of determining fluorine in a diversity of materials.<sup>2-8</sup> In the past the fluorine content of inorganic materials was normally determined by the Willard and Winter distillation method<sup>9</sup> and more recently by a pyrohydrolysis method.<sup>10</sup> Peters and Ladd<sup>7</sup> have applied the fluoride electrode to the analysis of several materials comprised of mixed oxides and have shown that the method of direct potentiometric measurement is faster (the distillation method requires the collection of a large volume of distillate)

1. McCAULEY, J. W. *Fabrication of Novel Composites - Part II: Fabrication and Properties of Ba-Mica/Al<sub>2</sub>O<sub>3</sub> Composites*. Army Materials and Mechanics Research Center, AMMRC TR 73-22, May 1973.
2. EDMOND, C. R. *Direct Determination of Fluoride in Phosphate Rock Samples Using the Specific Ion Electrode*. Anal. Chem., v. 41, 1969, p. 1327-1328.
3. FRANT, M. S., and ROSS, J. W., Jr. *Use of a Total Ionic Strength Adjustment Buffer for Electrode Determination of Fluoride in Water Supplies*. Anal. Chem., v. 40, 1968, p. 1169-1171.
4. INGRAM, B. L. *Determination of Fluoride in Silicate Rocks Without Separation of Aluminum Using a Specific Ion Electrode*. Anal. Chem., v. 42, 1970, p. 1825-1827.
5. KE, P. J., and REGIER, L. W. *Direct Potentiometric Determination of Fluoride in Water After 8-Hydroxyquinoline Extraction*. Anal. Chim. Acta, v. 53, 1971, p. 23-29.
6. OLIVER, R. T., and CLAYTON, A. G. *Direct Determination of Fluoride in Miscellaneous Fluoride Materials With the Orion Fluoride Electrode*. Anal. Chim. Acta, v. 51, 1970, p. 409-415.
7. PETERS, M. A., and LADD, D. M. *Determination of Fluoride in Oxides With the Fluoride-Ion Activity Electrode*. Talanata, v. 18, 1971, p. 655-664.
8. VAN LOON, J. C. *The Rapid Determination of Fluoride in Mineral Fluorides Using a Specific Ion Electrode*. Analytical Letters, v. 1, 1968, p. 393-398.
9. WILLARD, H. H., and WINTER, O. B. *Volumetric Method for the Determination of Fluorine*. Ind. Eng. Chem., Anal. Ed., v. 5, 1933, p. 7-10.
10. CLEMENTS, R. R., SERGEANT, G. A., and WEBB, P. J. *The Determination of Fluorine in Rocks and Minerals by a Pyrohydrolytic Method*. Analyst, v. 96, 1971, p. 51-54.

than and as accurate as the distillation or pyrohydrolysis methods. Of particular interest for the present application is the work of Oliver and Clayton<sup>6</sup> who showed that direct potentiometry using the fluoride electrode can be applied at pH 12 without interference from relatively high concentrations of aluminum since hydroxide ions complex aluminum much more strongly at this pH than do fluoride ions.<sup>11</sup>

Since the composites to be analyzed nominally contain 50 to 90 percent by volume of alumina, advantage was taken of this approach to establish a rapid and simple method for determining fluorine in these materials and in fluomicas as well. Due to the lack of standard or reference materials of similar compositions, potentiometric measurements were also made at pH 8, in this case with complexing and buffering agents added, and various methods of sample decomposition and preparation were employed, to provide a measure of the reliability of the proposed method.

## EXPERIMENTAL

### A. Equipment and Reagents

#### Equipment

Potential measurements were made with an Orion Model 801 digital pH meter in conjunction with an Orion Model 94-09 fluoride electrode and Model 90-01 single junction reference electrode.

#### Reagents

All reagents were of analytical reagent grade quality.

#### 1,2-Diaminocyclohexane-Tetraacetate-Sodium Chloride (DCTA-NaCl) Solution.

35.3 g of DCTA were added to 600 ml of water and 40 percent sodium hydroxide was added slowly while stirring until the DCTA dissolved. After addition of 120 g of NaCl the pH was adjusted to 8 with hydrochloric acid and the solution was diluted to a final volume of 1 liter. This solution was approximately 2 M in sodium chloride and 0.12 M in DCTA.

Fluoride Standard Stock Solutions. A 0.1-M fluoride stock solution was prepared by dissolving 2.100 g of sodium fluoride (which had been dried for 2 hours at 120 C) in 300 ml of water. The solution was diluted to 500 ml in a volumetric flask. This solution was diluted ten-fold to prepare a 0.01-M fluoride stock solution. Calibration solutions were prepared by taking appropriate aliquot portions of the 0.01-M fluoride solution.

All solutions, including calibration and sample solutions, were transferred to plastic bottles for storage immediately after preparation.

11. RINGBOM, A. *Complexation in Analytical Chemistry*. Interscience Publishers, New York, 1963, Tables A.5, A.2a, and A.2d, p. 352, 298, 310.

## B. Preparation of Samples and Standards for Measurements at pH 8

### Sodium Carbonate-Sodium Borate Fusion

Oliver and Clayton<sup>6</sup> determined the fluoride content of alumina containing one percent of aluminum fluoride by employing two different methods of sample decomposition: fusion with  $\text{Na}_2\text{CO}_3$  alone (3 g for a 0.5 g sample), and fusion with a 2 g:1 g  $\text{Na}_2\text{CO}_3$ - $\text{Na}_2\text{B}_4\text{O}_7$  mixture. In both cases there was no evidence of fluoride loss due to the fusion process. Potentiometric measurement with the fluoride electrode was made at pH 8 following dissolution of the melt in water and an ionic strength buffer. Standards were prepared by making known additions of sodium fluoride to solutions of fluoride-free alumina which had been prepared by fusion with sodium carbonate, and treating in the same manner as the samples. The authors point out that the only difference in the results is that the borate flux yields a completely soluble melt. Their ionic strength adjustment buffer contained 0.5 M potassium chloride, 0.5 M potassium acetate, and 1 M sodium citrate, the concentration of the latter being made high to insure effective complexation of aluminum at the high concentrations encountered in most of the samples tested. However, the concentration of these reagents in the final solution is not known since the dilution ratio of buffer to sample is not indicated.

For the determination of fluoride in oxide samples relatively high in aluminum content, Peters and Ladd<sup>7</sup> used a fusion mixture of 6 g  $\text{Na}_2\text{O}_2$  and 4 g  $\text{Na}_2\text{CO}_3$  for sample decomposition. They investigated the possibility of fluoride loss during treatment with the hot flux (900 C) by comparing results with those obtained by a low-temperature (520 C) decomposition method. There was no indication of fluoride loss due to volatilization at the higher temperature. These authors employed a complexing buffer solution containing 1 M sodium citrate, 1 M sodium chloride, and 0.06 M of DCTA. Their measurements were made at pH 6 and the complexing buffer solution comprised 50 percent of the final measured solution. The above reagent concentrations were thus reduced to 0.5 M, 0.5 M, and 0.03 M, respectively.

In the present work, a preliminary interference study was first made using the complexing buffer solution of Peters and Ladd.<sup>7</sup> However, measurements were made at pH 8 since at this pH citrate is more effective at complexing aluminum.<sup>11</sup> The presence of 500 ppm of aluminum caused a significant difference in the measured potential of a  $5 \times 10^{-4}$  M fluoride solution as compared with standards containing no aluminum, even when the citrate concentration in the measured solution was increased from 0.5 M to 0.85 M. At this higher citrate concentration the maximum tolerable aluminum concentration was found to be about 300 ppm in order to keep the difference between the measured potentials (due to the presence of aluminum) below 1 millivolt. On the basis of this finding and the nominal composition of the composites, a sample concentration of  $50 \pm 5$  mg per 100 ml was chosen for subsequent measurements at pH 8. At this sample concentration, further interference studies showed that the resultant concentrations of barium, magnesium, and silicon (based on the composition of the barium fluomica used to prepare the composites) would have no effect on the electrode measurements.



Composite samples were initially ground in a tungsten carbide mill. Portions weighing  $200 \pm 20$  mg (accurately weighed) were decomposed by fusing with a mixture of 2 g of  $\text{Na}_2\text{CO}_3$  and 1 g of  $\text{Na}_2\text{B}_4\text{O}_7$  in covered platinum crucibles. The melts were leached in dilute hydrochloric acid to obtain clear solutions which were diluted to a final volume of 100 ml. (Volumetric flasks were used for all final volume adjustments.) To 25-ml aliquots of these solutions were added 25 g of sodium citrate dihydrate and 15 ml of water. After dissolving most of the salt by swirling, the pH was adjusted to  $8 \pm 0.1$  by dropwise addition of a 30% solution of sodium hydroxide. At this point 25 ml of the DCTA-NaCl solution were added and the final volumes adjusted to 100 ml. (If the DCTA is added before pH adjustment, it is converted to the acid form which reacts quite slowly with sodium hydroxide making subsequent pH adjustment cumbersome.)

Standard fluoride solutions used for calibration were prepared to contain approximately the same concentration of aluminum as the samples. (The concentration in the samples ranged from about 180 to 250 ppm, that of the standards was 220 ppm.) A 327-mg portion of fluoride-free alumina powder was decomposed and dissolved in the same manner as the samples except that twice the amount of flux and dilute hydrochloric acid were used and the final volume was adjusted to 200 ml. Appropriate portions of the sodium fluoride stock solution were added to 25-ml aliquots of this solution to prepare six standards covering the range of  $2 \times 10^{-4}$  to  $1.5 \times 10^{-3}$  M in fluoride concentration. In each case additions of citrate and DCTA, with intermediate pH adjustment, were made in the same manner as the samples. The solutions were then diluted to 100 ml and mixed thoroughly. A series of standards containing no aluminum and no borate were also prepared to evaluate their combined effect on the calibration curve.

#### Sodium Carbonate Fusion

Because it is ineffective in decomposing alumina, fusion of samples rich in alumina with sodium carbonate results in much of the samples remaining undissolved. However, when this method of decomposition was applied to samples consisting almost entirely of alumina, no loss of fluoride occurred.<sup>6</sup> If the melt is leached in water, elements forming insoluble carbonates and hydroxides are precipitated from the highly alkaline solution (pH 12). Even in this situation, little or no loss of fluoride occurs due to occlusion or coprecipitation.<sup>6,7</sup> In the present application, it was desired to confirm the quantitative recovery of fluoride following fusion with sodium carbonate by comparing the results of this approach with those obtained using the carbonate-borate mixture for sample decomposition, in which case the samples were completely solubilized. In order to be able to distinguish between the effect, if any, of incomplete decomposition and that of carbonate and hydroxide precipitation, both a water and acid leach of the fusion melts were employed.

The composites (200 mg) were fused with 2 g of  $\text{Na}_2\text{CO}_3$ , and 200-mg portions of barium fluomica (-325 mesh, as received) were fused with 4 g of  $\text{Na}_2\text{CO}_3$ . One set was leached in water, the other in dilute hydrochloric acid. The composite sample solutions were diluted to a final volume of 100 ml and the fluomica solutions to 200 ml. After allowing the undissolved material to settle (in plastic bottles), 25-ml aliquots were treated with citrate and CDTA and the pH was adjusted as previously described. However, an amount of dilute hydrochloric acid was initially added to the portions taken from the water-leached samples such that the acid concentration would be the same in all samples. The solutions were then diluted to 100 ml and mixed.

For the preparation of standards, a stock solution of  $\text{Na}_2\text{CO}_3$  was used. Ten g were dissolved in dilute hydrochloric acid (35 ml of  $\text{HCl}$  and 300 ml of water), the pH was adjusted to 8, and the solution was diluted to 500 ml. After making known additions of fluoride to 25-ml aliquots of the  $\text{Na}_2\text{CO}_3$  stock solution, preparation of the standard solutions was completed in the usual manner.

#### C. Preparation of Samples and Standards for Measurements at pH 12

For the high pH measurements, two methods of sample preparation were employed. In the one case, 250- to 300-mg samples were fused with 2 g (composites) and 4 g (barium fluomica) of  $\text{Na}_2\text{CO}_3$ . After leaching in water, the composite sample solutions were diluted to 100 ml and the barium fluomica solutions to 200 ml. When the undissolved residue had settled, 30-ml aliquots were diluted to 100 ml, mixed and reserved for subsequent measurement.

In the second case, 300- to 400-mg samples were fused with 3 g (composites) and 6 g (fluomica) of  $\text{Na}_2\text{CO}_3$ . The melts were leached in 400 ml and 800 ml of water, respectively, after which the solutions were diluted to 500 ml and 1 liter. After settling, approximately 100 ml of the supernatant solution were decanted into a Teflon beaker for the potentiometric measurements.

Calibration solutions were prepared by adding aliquot portions of the sodium fluoride stock solution to 50-ml portions of a stock  $\text{Na}_2\text{CO}_3$  solution containing 6 g of the prefused salt in 500 ml of solution. The solutions were diluted to a final volume of 100 ml.

#### D. Potentiometric Measurements

All measurements were made using a 250-ml Teflon beaker to contain the analyte. The nonwetting nature of the Teflon made it convenient to rinse and wipe the beaker dry when changing from one solution to the next. Electrodes were also rinsed and patted dry between measurements. A Teflon-coated magnetic stirring bar was used to stir the solution throughout each measurement. The magnetic stirrer was fitted with a glass top, which served to minimize the conduction of heat from the stirrer motor to the sample. The stirring rate was set to provide adequate mixing but excessive rates were avoided to prevent the collection of bubbles on the electrodes.

As nearly as possible, measurements were made in the order of increasing fluoride concentration, starting with lowest concentrations. For each series of measurements, about an hour was required for the initial reading to allow the system to equilibrate and provide a stable readout. Subsequent readings were taken 15 minutes after immersion of the electrodes.

## RESULTS AND DISCUSSION

Calibration curves were prepared by plotting the potentiometric readings (in millivolts) of the fluoride standards versus the logarithm of the fluoride concentration (in molarity). At pH 8, standards containing no aluminum and no borate yielded a perfectly straight calibration curve. Standards containing aluminum and sodium borate produced a parallel curve up to  $7 \times 10^{-4}$  M fluoride which was shifted in the positive direction by 1.6 mV. The effect of borate alone was evaluated and found to cause a similar positive shift, indicating that the effect of aluminum (at the 220-ppm level) is negligible at fluoride concentrations below  $7 \times 10^{-4}$  M. At higher fluoride levels, however, the curves began to diverge to a difference of 3.0 mV at  $1.5 \times 10^{-3}$  M fluoride. Apparently at this point ( $7 \times 10^{-4}$  M) fluoride begins to complex aluminum in competition with citrate. A similar effect at about  $5 \times 10^{-4}$  M fluoride was noted by Oliver and Clayton.<sup>6</sup> The important point demonstrated here is that the standards should contain borate and aluminum (at fluoride concentrations above  $7 \times 10^{-4}$  M) in amounts equivalent to those of the samples when the carbonate-borate flux is used for sample decomposition.

Based on the measurements at pH 8, the recovery of fluoride from the samples was essentially the same regardless of the method of sample decomposition and preparation. This includes the carbonate-borate fusion, and the sodium carbonate fusion with both acid and water leaches. Apparently fusion with sodium carbonate did not result in loss of fluoride due to incomplete decomposition (alumina) or precipitation of barium carbonate and magnesium hydroxide (water leach).

At pH 12, the response of the fluoride electrode began to deviate from linearity at fluoride concentrations below  $7 \times 10^{-4}$  M. At this point the electrode begins to respond to the hydroxyl ion. Down to  $3 \times 10^{-4}$  M fluoride the deviation is slight but below this the effect becomes quite pronounced making measurements below this level unreliable. Oliver and Clayton,<sup>6</sup> working with the same medium (aqueous sodium carbonate), found the onset of hydroxyl-ion interference to occur at about  $5 \times 10^{-4}$  M fluoride.

Using the much simpler method of fusion with sodium carbonate, leaching in water, and measuring at pH 12, the recovery of fluoride from the samples was the same as that obtained at pH 8. Table 1 lists the values obtained, in weight percent, at pH 8 and pH 12. Also listed are the average values and the overall standard deviations.

The standard deviation values obtained are typical for the direct potentiometric method using the fluoride electrode. In determining one percent of aluminum fluoride in alumina, Oliver and Clayton reported standard deviations ranging from 0.021 to 0.077. The standard deviations in Table 1 amount to about one to four percent of the fluoride values.

Table 1. FLUORIDE RESULTS AT pH 8 AND pH 12, WEIGHT PERCENT

| Composites  |      | pH 8                                                                                     |                                           | pH 12                                     |                | Over-<br>all<br>Avg. | Overall<br>Standard<br>Deviation |
|-------------|------|------------------------------------------------------------------------------------------|-------------------------------------------|-------------------------------------------|----------------|----------------------|----------------------------------|
|             |      | Na <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub><br>Fusion | Na <sub>2</sub> CO <sub>3</sub><br>Fusion | Na <sub>2</sub> CO <sub>3</sub><br>Fusion |                |                      |                                  |
|             |      | Acid<br>Leach                                                                            | Acid<br>Leach                             | Water<br>Leach                            | Water<br>Leach |                      |                                  |
| A           |      | 0.83                                                                                     | 0.85                                      | 0.90                                      | 0.89           |                      |                                  |
|             |      | 0.87                                                                                     | 0.87                                      | 0.87                                      | 0.87           |                      |                                  |
|             | Avg. | 0.85                                                                                     | 0.86                                      | 0.88                                      | 0.88           | 0.87                 | 0.021                            |
| B           |      | 1.37                                                                                     | 1.33                                      | 1.35                                      | 1.44           |                      |                                  |
|             |      | 1.46                                                                                     | 1.43                                      | 1.35                                      | 1.46           |                      |                                  |
|             | Avg. | 1.41                                                                                     | 1.38                                      | 1.38                                      | 1.45           | 1.40                 | 0.053                            |
| C           |      | 2.41                                                                                     | 2.43                                      | 2.38                                      | 2.40           |                      |                                  |
|             |      | 2.47                                                                                     | 2.43                                      | 2.46                                      | 2.39           |                      |                                  |
|             | Avg. | 2.44                                                                                     | 2.43                                      | 2.43                                      | 2.39           | 2.43                 | 0.033                            |
| D           |      | 3.78                                                                                     | 3.82                                      | 3.74                                      | 3.80           |                      |                                  |
|             |      | 3.82                                                                                     | 3.87                                      | 3.83                                      | 3.89           |                      |                                  |
|             | Avg. | 3.80                                                                                     | 3.84                                      | 3.80                                      | 3.85           | 3.82                 | 0.045                            |
| Ba Fluomica |      |                                                                                          | 10.87                                     | 10.69                                     | 11.15          |                      |                                  |
|             |      |                                                                                          | 10.70                                     | 10.91                                     | 10.67          |                      |                                  |
|             | Avg. |                                                                                          | 10.78                                     | 10.94                                     | 10.91          | 10.87                | 0.215                            |

Based on the original mixtures of fluomica and alumina used to prepare the analyzed composites, the indicated fluoride losses range from about 20 percent at the low level to 30 percent at the high level. Test specimens of the analyzed composites proved to be entirely satisfactory, exhibiting the desired linear relationship between physical properties and alumina content.\* Apparently, the loss of fluoride to the extent indicated can be tolerated without fear of excessive phase degradation. Obviously the direct potentiometric determination of fluoride is more than adequate to monitor such fluoride losses and to assure that these levels are not exceeded.

In applying the recommended method of fusion with sodium carbonate and measurement at pH 12 (see Appendix for detailed procedure), the sodium carbonate stock solution used for the standards must be prepared with the pre-fused salt to insure that the hydroxyl-ion concentration of the standards and samples is the same. Due to partial decomposition of carbonate to oxide during prolonged fusion, the pH of the fused-salt solution is measurably higher (0.3 unit) than that of the unfused salt. This small difference has a significant effect on the calibration curve obtained.

\*Private Communication, Dr. J. W. McCauley, Army Materials and Mechanics Research Center.

Table 2 lists the fluoride results obtained for the samples using fused and unfused salt to prepare the standards. For the latter the averages of two determinations are shown. For the former the sodium carbonate (6 g) was fused in a covered platinum crucible at maximum gas burner heat (about 900 C) for one hour after initial melting over an intermediate flame.

| Table 2. EFFECT OF<br>SODIUM CARBONATE FUSION ON FLUORIDE RESULTS |                          |         |
|-------------------------------------------------------------------|--------------------------|---------|
| Composites                                                        | Fluoride, Weight Percent |         |
|                                                                   | Fused                    | Unfused |
| A                                                                 | 0.88                     | 1.41    |
| B                                                                 | 1.45                     | 2.65    |
| C                                                                 | 2.39                     | 3.87    |
| D                                                                 | 3.85                     | 5.68    |
| Ba Fluomica                                                       | 10.91                    | 11.88   |

In every case the result obtained with the unfused-salt standards is significantly higher. However, extending the fusion time to two hours had no effect on the calibration curve obtained with the fused-salt standards. Apparently an equilibrium condition is approached following initial decomposition of the sodium carbonate after which the decomposition rate is negligibly slow. Obviously, to minimize and control the extent of decomposition, all fusions should be performed in covered crucibles.

In summary, direct potentiometric measurement with the fluoride electrode in a sodium carbonate medium offers a simple and rapid means for the determination of fluoride in fluomica and fluomica composites. The preparation of samples and standards is simple and straightforward since the addition of complexing and buffering agents is not required nor is the adjustment of pH necessary. Hydroxyl-ion interference is easily avoided by adjusting the sample size to keep the fluoride concentration above  $3 \times 10^{-4}$  M.

#### RECOMMENDATION

It is recommended that the direct potentiometric method for the determination of fluoride using the fluoride electrode, details of which are given in the APPENDIX, be included in Army purchase descriptions for materials and products composed of fluomica and fluomica composites.

APPENDIX. DETAILED PROCEDURE FOR THE DETERMINATION  
OF FLUORIDE IN FLUOMICA AND FLUOMICA COMPOSITES

1. Scope of Method

This method covers the determination of fluoride in fluomica composites in the range from 0.8 to 4.5 percent and in fluomica in the range from 2.5 to 11 percent. Lower levels of fluoride can be determined by increasing the sample size, provided the measured fluoride concentration is not less than  $3 \times 10^{-4}$  M. Higher levels can be determined by dilution of the sample solutions beyond the recommended volumes, provided the amount of sodium carbonate is proportionately increased to maintain its concentration at the recommended level (6 g/l).

2. Procedure

a. Preparation of Samples. Accurately weigh  $400 \pm 50$  mg of composite samples and  $300 \pm 40$  mg of fluomica samples into platinum crucibles. Add 3 g of  $\text{Na}_2\text{CO}_3$  to the former and 6 g of  $\text{Na}_2\text{CO}_3$  to the latter. After mixing, cover the crucibles with snug-fitting platinum covers and place the crucibles over gas burners previously adjusted to a low flame. Gradually increase the applied heat to melt the flux slowly, then fuse at maximum burner temperature for one hour with occasional swirling (a Claiss stirrer can be used to provide constant swirling during fusion).

After cooling, transfer the covered crucibles to Teflon beakers containing sufficient water to submerge the crucibles. Heat on a hot plate with occasional stirring to dissolve the soluble salts, taking pains to insure that the undissolved material (alumina, magnesium hydroxide, and calcium carbonate) is not hiding any hard pieces of undecomposed melt. After cooling, remove and wash the crucibles and covers. Dilute the composite sample solutions to 500 ml and the fluomica solutions to 1 liter, using volumetric flasks. After mixing thoroughly, transfer immediately to plastic bottles.

b. Preparation of Calibration Standards. Prepare a stock  $\text{Na}_2\text{CO}_3$  solution by fusing 6 g of the salt for one hour in a covered platinum crucible. Leach the fused salt in water in the same manner as described above. Dilute the solution to 500 ml, mix, and store in a plastic bottle. Transfer 50-ml aliquots of this solution to six 100-ml volumetric flasks, using a pipet. Add to successive flasks, again using pipets, 3, 5, 7, 10, 15, and 20 ml of the 0.01 M fluoride stock solution. Dilute to volume, mix, and transfer to plastic bottles.

c. Potentiometric Measurements. As nearly as possible, make measurements in the order of increasing fluoride concentration, starting with the lowest standard ( $3 \times 10^{-4}$  M fluoride). If necessary, make repeat measurements to conform with this order. The fluoride electrode displays a memory effect which retards equilibration when passing from higher to lower fluoride concentrations. In any event, up to an hour may be required to obtain a stable readout for the

initial measurement. Subsequent readings may stabilize in five to ten minutes, especially at higher fluoride concentrations, but it has been our practice to record measurements fifteen minutes after electrode immersion to allow for occasional slow responses.

To make the measurement, transfer about 100 ml of the solution to a clean, dry Teflon beaker containing a Teflon-coated magnetic stirring bar. Place the beaker on a magnetic stirrer fitted with a glass top to minimize heat transfer to the sample (or place a piece of asbestos beneath the beaker). Set the stirring rate to provide adequate mixing and immerse the electrodes. Move the function knob of the meter from standby to read millivolts. Between measurements, turn the function knob to standby, then rinse and dry the electrodes.

d. Calculation of Results. Using semilogarithmic graph paper, plot the potential readings of the standards on the linear scale versus the corresponding fluoride concentrations on the logarithmic scale to prepare the calibration curve. Referring to the calibration curve, determine the fluoride concentration of the samples from the potential readings obtained.

Calculate the weight percent of fluoride as follows:

$$\text{Fluoride, weight percent} = \frac{A \times B \times 1900}{C}$$

where:

A = fluoride concentration, molarity,

B = final dilution volume of sample solution, and

C = weight of sample, in milligrams.

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