

microbiological contamination, the use of modified atmospheres on primal or subprimal cuts of beef may demonstrate even better results.

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An Ion-Specific Electrode Analysis of Fluoride in Potato Tops Using an Ion-Exchange Pretreatment

A method for fluoride determination is developed which utilizes a hot-water extraction of inorganic F⁻ from dried potato tops. The interferences of F⁻ complexing species are effectively removed with an ion-exchange pretreatment, followed by a relatively simple specific-ion electrode determination. Recovery of F⁻ varied from 99–103%, compared to the AOAC procedure.

The use of a fluoride-specific electrode has become a convenient and economical tool for many types of samples, ranging from impurities in aluminum (Palmer, 1972) to contaminants in feeds (Torma, 1975) and plant matter (Baker, 1972; Vickery and Vickery, 1976). These procedures all have the common problem of complexation of fluoride by metals and hydrogen ions. The approach to solving this problem has been to find a complexing agent which will tie up the metals, buffer the solution to the correct range, and free fluoride ions, the only species to which the electrode responds (Durst, 1969). In this paper, a different approach is presented, that being to remove these metals by ion exchange, buffer the solution, and then determine the fluoride content.

EXPERIMENTAL SECTION

Apparatus. The fluoride-specific electrode was an Orion Research Model 94-09, and the reference electrode was an Orion Research Model 90-02 double-junction electrode. The pH meter used was a Beckman SS-1, with expanded millivolt scale.

Reagents. A 1000 µg/mL standard fluoride stock solution was made from reagent grade anhydrous potassium fluoride. Total ionic strength adjuster (TISAB) solution was made from reagent grade glacial acetic acid, sodium chloride, CDTA (cyclohexylenedinitrilotetraacetic acid), and sodium hydroxide according to the electrode manufacturer's instructions. Solutions of Al and Fe, 1000 µg/mL, were purchased from Fisher Scientific.

The ion-exchange resin used was Amerlite CG-120, 100–200 mesh. The resin was first washed in 7 N NH₄OH and then water washed until neutral. Next, it was washed in 6 N HCl and again washed with distilled water until neutral. The resin was stored in distilled water until used.

Procedure. The samples used for this study were potato tops which had been dried in open air sunlight for 1 week. The vegetation was then crushed to fit in gallon

jars and dried at 105 °C for 48 h. The samples were then ground in an Osterizer finely enough to pass through an 80 mesh (180 µm) screen.

One-gram samples of these tops were extracted with 25 mL of distilled water on a steam bath for 30 min. The extracts were then filtered through glass fiber filters into a 50-mL volumetric flask and then diluted to volume with distilled water.

Ten milliliters of this solution were then placed onto 5 g of Amberlite which was packed in a 50-mL buret. The sample was washed off the column with an additional 15 mL of water. The column was eluted into another 50 mL volumetric flask which contained 25 mL of the TISAB solution. The contents were mixed, and the fluoride content was determined with the fluoride electrode according to the manufacturer's instructions.

The ion-exchange resin was then stripped by washing 5 mL of 7 N NH₄OH onto the column and washing with distilled water until the eluent was neutral to litmus paper. The resin was then recharged by washing 5 mL of 6 N HCl onto the column, and the distilled water wash was repeated until the eluent was again neutral. The same resin was used in this manner for three samples before discarding. The electrode calibration was done without ion-exchange pretreatment and covered the range from 0.1 to 20 µg/mL.

RESULTS AND DISCUSSION

A calibration curve was constructed to cover a wide range of concentrations since the approximate fluoride concentration of the potato tops were not known. The range covered was 0.1 to 20 µg/mL. The calibration gave a straight line with a slope of -57.8 (which indicates Nernstian behavior) and a correlation coefficient (*r*²) of 99.98%.

Recovery studies of F⁻ through the ion-exchange column were conducted using 10-mL aliquots of 5, 10, and 20 µg/mL of F⁻ standard solutions. After ion exchange, the

**Table I. Fluoride Content of Potato Top Samples
F⁻ Concentration**

Sample no.	Test solution, $\mu\text{g/mL}$	Bulk, $\mu\text{g/g}$	Percent RSD ^a
1-A	0.27	67.5	
1-B	0.30	75.0	5.4
1-C	0.28	70.0	
2-A	0.19	47.5	
2-B	0.21	52.5	7.4
2-C	0.22	55.0	
3	0.21	52.5	
4	0.20	50.0	
5	0.23	57.5	
6	0.26	65.0	
7	0.27	67.5	
8	0.28	70.0	
9	0.28	70.0	
10	0.31	77.5	
11	0.31	77.5	
12	0.30	75.0	
13	0.26	65.0	
14	0.27	67.5	
15	0.23	57.5	
16	0.12	30.0	

^a RSD = relative standard deviation.

resulting F⁻ concentrations should be 1, 2, and 4 $\mu\text{g/mL}$, respectively. The amounts found were 0.92, 1.98, and 4.07 $\mu\text{g/mL}$, respectively.

Since aluminum and iron are considered the most serious interferences in the F⁻ determination, the Al and Fe contents of the samples were determined by atomic emission spectrography. The Al concentrations of the potato tops varied on a dry weight basis from 180 to 850 $\mu\text{g/g}$, and the Fe varied from 160 to 560 $\mu\text{g/g}$. At these levels, the final concentrations of Al and Fe in a test solution without any other treatment would be about 3 to 17 $\mu\text{g/mL}$, depending on the sample. Assuming the respective test solution contained 1 $\mu\text{g/mL}$ of F⁻, the complexation of Al and Fe would be incomplete in the CDTA buffer system described (Orion Research, 1975).

Ion exchange, thus, appeared to be a convenient method to remove Al and Fe; at least, to a very low or manageable level with respect to the CDTA buffer system. To determine the amount of Al and Fe left in a test solution after ion exchange, an atomic absorption determination of these two metals was made using the sample containing the highest level of the respective element. In both cases, neither Al nor Fe could be detected.

To determine the amount of F⁻ that might remain on the ion-exchange column as a positively charged complex, 100 $\mu\text{g/mL}$ of both Al and Fe were added to 5, 10, and 20 $\mu\text{g/mL}$ of F⁻ standards. Each solution was allowed to equilibrate for 1 h before ion-exchange treatment (Srinivasan and Rechnitz, 1968). After the ion-exchange treatment, the eluent was again tested for Al and Fe and the F⁻ content determined. There was no Al or Fe detected while the F⁻ concentrations were 1.01, 2.03, and 3.95 $\mu\text{g/mL}$, respectively, indicating no F⁻ retention on the column.

The fluoride levels of a number of sample test solutions were done, showing a concentration range through the samples of 0.1–0.3 $\mu\text{g/mL}$. Two samples of this lot were

**Table II. Comparison of the Two Methods
F⁻ Concentration ($\mu\text{g/g}$)**

Sample no.	This paper	AOAC	Percent RSD, AOAC
1-A	67.5	68.3	
1-B	75.0	74.8	5.1
1-C	70.0	68.9	
4	50.0	51.1	
8	70.0	72.0	
9	70.0	70.1	
12	75.0	76.3	
16	30.0	29.7	

run in triplicate to assess internal precision. The results are included in Table I. The mean deviation of both sets of triplicate test solutions was 1%.

To determine the accuracy of this method, five samples were selected at random and run by the AOAC official method (Torma, 1975). The results are shown in Table II. The percent difference between the two methods appears to be no greater than 3% on a relative basis. In addition, the method developed here also required less time for electrode equilibration (2 min compared with 10 or 15 min) and gave equally reproducible results (see Table II).

The differences are not attributable to any one cause (i.e., high Al or Fe content) and are probably due to a combination of factors which include extraction method, pH of the buffer, and stability of the metal complex which releases fluoride for detection at the electrode.

The method developed here does show good reproducibility and does eliminate interferences, such as Al and Fe, to give confidence that none of the F⁻ is complexed, especially when these interferences are unknown or cannot be determined. Furthermore, because of the good agreement between the AOAC procedure and the one developed here, it can be concluded that F⁻ can be adequately determined in potato tops, and perhaps other types of vegetation, using relatively standard equipment and laboratory techniques.

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