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## Novel ethyl-derivatization approach for the determination of fluoride by headspace GC/MS

Enea Pagliano<sup>a,b,\*</sup>, Juris Meija<sup>a</sup>, Jianfu Ding<sup>a</sup>, Ralph E. Sturgeon<sup>a</sup>, Alessandro D'Ulivo<sup>c</sup>, and Zoltán Mester<sup>a</sup>

<sup>a</sup> National Research Council of Canada, 1200 Montreal Road, Ottawa, ON K1A 0R6, Canada.

<sup>b</sup> Scuola Normale Superiore, Piazza dei Cavalieri, 7, 56126, Pisa, Italy.

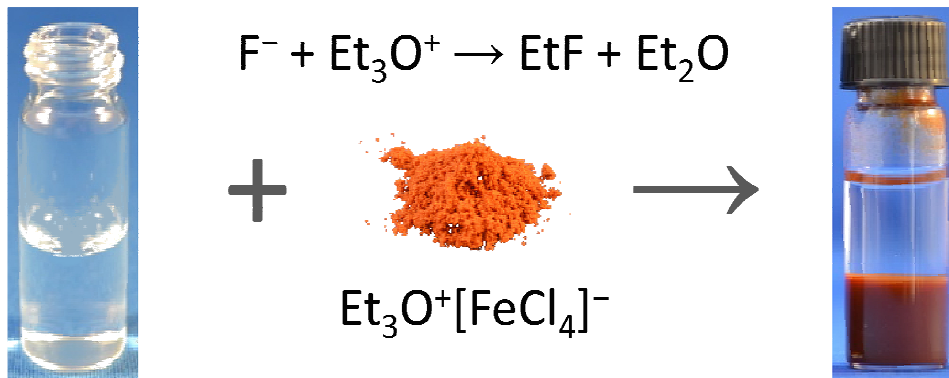
<sup>c</sup> CNR, Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici, Via G. Moruzzi, 1, 56124 Pisa, Italy.

\* Corresponding author. e-mails: <[enea.pagliano@nrc-cnrc.gc.ca](mailto:enea.pagliano@nrc-cnrc.gc.ca)> and <[e.pagliano@libero.it](mailto:e.pagliano@libero.it)>

### ABSTRACT

We report a novel derivatization chemistry for determination of fluoride based on batch reaction of fluoride ions with triethyloxonium tetrachloroferrate(III) in a closed vessel to yield fluoroethane. Gaseous fluoroethane was readily separated from the matrix, sampled from the headspace and determined by gas chromatography/mass spectrometry. The method was validated using rainwater certified reference material (IRMM CA408) and subsequently applied to the determination of fluoride in various matrices, including tap water, seawater, and urine. An instrumental limit of detection of 3.2 µg/L with a linear range up to 50 mg/L was achieved. The proposed derivatization is a one-step reaction, requires no organic solvents and is safe, as the derivatizing agent is nonvolatile. Determination of fluoride is affected by common fluoride-complexing agents, such as Al(III) and Fe(III). The effect of large amounts of these interferences was studied and the adverse effect of these ions was eliminated by use of the method of standard additions.

### Graphic Abstract



## INTRODUCTION

A large number of municipalities in North America supplement their drinking water with fluoride as it prevents tooth decay owing to its cariostatic activity. Ensuing debates over the efficacy of fluoridation notwithstanding, accurate monitoring of fluoride is of importance in countries where water fluoridation is practiced.<sup>1-4</sup> Due to the toxic effects of fluoride at higher concentrations, a guideline value of 1.5 mg/L is recommended by the World Health Organization as a level at which dental fluorosis should be minimal.<sup>5</sup> Considering also that elevated levels of fluoride occur in natural waters over an extensive geographical belt, reaching well above 10 mg/L in some regions of Kenya<sup>6</sup> and India,<sup>7</sup> the monitoring of fluoride in water and food products is important from a toxicological point-of-view.

Fluorine, like boron, does not enter into chemical reactions that are selective enough to permit its direct determination in the presence of concomitant elements.<sup>8-9</sup> Consequently, no direct or specific spectrophotometry or fluorescence methods are available for its quantitation.<sup>10-13</sup> A significant advance in the determination of fluoride was development of the fluoride ion-selective electrode in 1966.<sup>14</sup> Owing to its simplicity, this has effectively become the method of choice for field and laboratory settings, providing a detection limit of ca. 20 µg/L.<sup>15</sup> However, ion-selective electrodes respond to the activity of fluoride ions, not to their concentration, and are affected by the presence of hydroxide ions.<sup>14</sup>

Modern instrumental methods can address the problem of measurement specificity. Fluorine can be determined by ICPMS, although poor sensitivity is reported (negative ion mode has been attempted yielding a detection limit of 110 µg/L<sup>16</sup>). Molecular absorption from ions such as GaF has been exploited for the determination of fluoride using high resolution continuum source atomic absorption spectrometry with reported detection limits close to 1 µg/L.<sup>17-18</sup> Similar figures of merit are reported for electrospray MS.<sup>19-20</sup>

Derivatization of fluoride ions has traditionally been performed using silicon-based chemistry in order to convert  $F^-$  to  $Me_3SiF^{21-22}$  or  $Ph_3SiF^{23}$ . The resulting volatile fluorosilanes can be determined by gas chromatography following either liquid extraction with organic solvents or solid-phase microextraction from the headspace, achieving a detection limit of 6  $\mu g/L$  in the latter case with  $Me_3SiF^{21}$ . However the Si–F bond in these derivatives is not stable in aqueous solutions, especially at high pH. Consequently, Kage et al.<sup>24</sup> proposed carbon-based alkylation of fluoride with pentafluorobenzylbromide ( $F_5BzBr$ ), yielding volatile  $F_5BzF$  which can be determined by GC/MS. Although stability of the resultant derivative is achieved, the method is limited by a poor detection limit (0.5 mg/L). Carbon-based derivatization of fluoride can also be achieved using tertiary oxonium salts. Despite their common use as alkylation agents in organic chemistry,<sup>25-26</sup> oxonium salts have only recently been introduced to the field of analytical chemistry.<sup>27-29</sup> The commercially available triethyloxonium tetrafluoroborate permits otherwise difficult alkylation reactions to be undertaken in aqueous media; in addition,  $Et_3O^+[BF_4]^-$  has been successfully applied for the derivatization of inorganic anions,<sup>27</sup> including chloride, bromide, iodide, cyanide, thiocyanate, sulfide, nitrite and nitrate.<sup>29</sup> Generation of volatile derivatives allows for the separation of the analyte from the matrix, thereby minimizing spectral interferences and reducing background levels in the separation and detection phase of the analysis.<sup>30</sup> However,  $Et_3O^+[BF_4]^-$  is not suitable for determination of fluoride because tetrafluoroborate slowly hydrolyzes, releasing fluoride ions. To overcome this drawback, the method proposed here employs triethyloxonium tetrachloroferrate(III) to convert fluoride to stable fluoroethane which can be subjected to analysis by GC/MS.

## EXPERIMENTAL SECTION

### Reagents and materials

Standard solutions of fluoride were prepared by dissolution of sodium fluoride (Baker;  $w = 0.999$  g/g) in deionized water generated with a MilliQ system. Anhydrous diethyl ether (Sigma-Aldrich), anhydrous iron(III) chloride (Sigma-Aldrich,  $w \geq 0.98$  g/g), and 2-(chloromethyl)-oxirane (Fluka,  $w = 0.99$  g/g; also known as ( $\pm$ )-epichlorohydrin) were used for the synthesis of triethyloxonium tetrachloroferrate(III). Triethyloxonium tetrafluoroborate (Fluka,  $w > 0.97$  g/g) and triethyloxonium hexachloroantimonate(VI) (Aldrich,  $w > 0.97$  g/g) were also sourced. An aqueous solution of ammonia (Tamapure AA-100;  $w(\text{NH}_3) = 0.2$  g/g) was used for adjustment of the pH of the sample. Rainwater, certified for fluoride content, was obtained from the Institute for Reference Materials and Measurements (CA408; Geel, Belgium). All other reagents were of analytical grade. Samples of different origin were also selected for testing: seawater (MOOS-2 certified reference material; NRC Canada), City of Ottawa drinking water, and urine from a healthy volunteer.

### Safety considerations

Despite widespread use of alkylation and silylation reactions for gas chromatography, the health risks of handling potentially toxic and volatile compounds, such as diazomethane, chloroformates or trimethylsilyl chloride, must be carefully considered.<sup>31</sup> Triethyloxonium tetrachloroferrate(III) is a strong ethylating agent and must be handled in a fume-hood with appropriate personal protective equipment. However, in comparison to other reagents used for derivatization, its potential toxicity is reduced because it is a nonvolatile crystalline salt which undergoes complete hydrolysis within 3 h.<sup>32</sup>  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$  is hygroscopic, but considerably less so than tetrafluoroborate and it should be stored in a freezer. In order to avoid excessive exposure to

ambient moisture, the bottle containing the reagent should be allowed to reach room temperature before opening and use of contents.

### **Triethyloxonium tetrachloroferrate(III)**

Triethyloxonium tetrachloroferrate(III) was synthesized according to the procedure of Meerwein et al:<sup>33</sup>



For this purpose, 0.2 mol (32.4 g) anhydrous  $\text{FeCl}_3$  was dissolved in 150 mL of dry diethyl ether. The headspace above the resultant solution was evacuated and purged with argon three times using a Schlenk line while keeping argon flowing during the reaction. During magnetic stirring, 0.1 mol (9.25 g) 2-(chloromethyl)oxirane was added drop-wise using a syringe. The addition of 2-(chloromethyl)oxirane was controlled to keep the ether under constant boiling. After this addition, the resultant mixture was further stirred for 5 min and then cooled to 0 °C using an ice/water bath and held at this temperature for 2 h with gentle magnetic stirring. The brown crystalline product was filtered on a Büchner funnel and subsequently washed twice with dry ether. A 23.2 g mass of  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$  was obtained (77% yield), enough to perform all the experiments described herein. Although the triethyloxonium tetrachloroferrate(III) is soluble in water, it slowly undergoes hydrolysis. Aqueous solutions of this salt should therefore be prepared shortly before use. In this work, the  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$  solutions were prepared by dissolving 0.4 g  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$  in 16 mL of MilliQ water.

### **Sample preparation**

A 2 mL volume of aqueous sample was introduced without pretreatment into five different vials, four of which were spiked with 0.2 mL of different fluoride standard solutions whereas 0.2 mL of

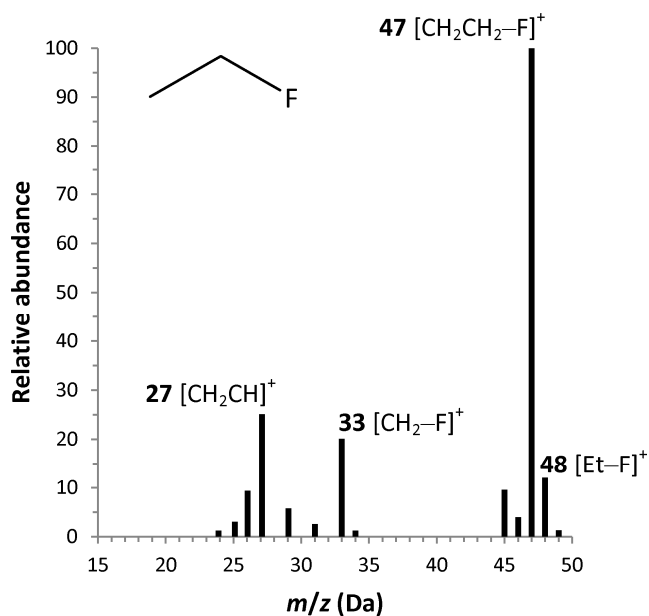
MilliQ water was added to the remaining vial. Quantitation of fluoride was based on the method of standard additions and the concentration of the standard was chosen so to obtain a maximum four-fold increase in the analytical signal compared to the non-spiked sample. The samples were spiked with a 50  $\mu\text{L}$  volume of ammonia solution ( $w(\text{NH}_3) = 0.2 \text{ g/g}$ ), and then with a 1 mL volume of the  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$  solution prepared as described above. After the addition of all reagents, the vials were quickly sealed with a screw-cap containing a PTFE/silicone septum and kept at room temperature for 3 h before sampling the headspace with a gas-tight syringe. Triethyloxonium converts  $\text{F}^-$  into fluoroethane which is gaseous at ambient temperature ( $t_{\text{vap}} = -37 \text{ }^\circ\text{C}$ ). Therefore, in order to avoid analyte loss, it is important that unpunctured septa be used for sealing.

### GC/MS analysis

A Hewlett-Packard 6890 gas chromatograph equipped with a Hewlett-Packard 5973 mass selective detector and fitted with a 60 m DB-624 column (6% cyanopropyl-phenyl 94% dimethyl polysiloxane) was operated at a constant flow of 0.9 mL He/min. Pulsed split (5:1) injection mode was chosen, with a pulsed pressure of 172 kPa for 1 min. The inlet temperature was set to 100  $^\circ\text{C}$ . After the first isotherm at 30  $^\circ\text{C}$  (held for 7 min), the oven was heated at 20  $^\circ\text{C}/\text{min}$  to 200  $^\circ\text{C}$ . The transfer line temperature was 230  $^\circ\text{C}$ . The generated fluoroethane was manually sampled with a gas-tight syringe from the vial headspace and a 250  $\mu\text{L}$  volume injected into the GC/MS. Fluoroethane eluted at 5 min under the 30  $^\circ\text{C}$  isotherm. In addition, chromatographic performance was improved with use of a narrow inlet liner (internal diameter of 0.75 mm) designed for SPME. The mass spectrometer was operated in electron impact mode (70 eV) using standard settings (ion source temperature 250  $^\circ\text{C}$ ; quadrupole temperature 150  $^\circ\text{C}$ ). The intensity of the fluoroethane molecular ion shown in Figure 1 is low (10% of the base peak); the most abundant fluorine-containing ions are  $\text{CH}_2\text{CH}_2\text{-F}^+$  ( $m/z = 47 \text{ Da}$ ) and  $\text{CH}_2\text{-F}^+$  ( $m/z = 33 \text{ Da}$ ). Therefore, quantitation



of fluoroethane was done by selected ion monitoring (SIM) using the area of the peak extracted at  $m/z = 47$  Da. The fragment ion at  $m/z = 33$  Da was monitored for quality control purposes. Both were acquired using a 100 ms dwell time.

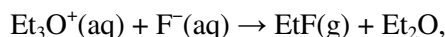


**Figure 1.** Electron impact mass spectrum of fluoroethane.

## RESULTS AND DISCUSSION

### Derivatization

The use of triethyloxonium salts as derivatizing reagents is a recent introduction to the field of analytical chemistry.<sup>27–29</sup> Unlike triethyloxonium tetrachloroferrate(III), which was selected for determination of fluoride in this work, the two commercially available oxonium salts,  $\text{Et}_3\text{O}^+[\text{BF}_4]^-$  and  $\text{Et}_3\text{O}^+[\text{SbCl}_6]^-$ , are unsuitable analytical reagents for conversion of fluoride to fluoroethane,



because  $\text{Et}_3\text{O}^+[\text{BF}_4]^-$  releases fluoride ions during hydrolysis of the tetrafluoroborate,<sup>34</sup> whereas  $\text{Et}_3\text{O}^+[\text{SbCl}_6]^-$  is not water soluble. Ethylation of fluoride with  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$  was performed in an alkaline medium (pH = 10) because an acidic environment releases Fe(III) from the salt which then binds to the fluoride ions. Additionally, the alkalinity of the sample causes precipitation of a number of endogenous metal ions, resulting in the removal of potential interferences in the determination of fluoride. Moreover, alkaline conditions prevent the conversion of fluoride to gaseous HF, a significant advantage compared to an acidic silylation method, wherein this may occur. The ethylation reaction stops after hydrolysis of  $\text{Et}_3\text{O}^+$  is complete. Granik et al.<sup>25</sup> reported that complete hydrolysis of  $\text{Et}_3\text{O}^+$  occurs in 80 min. From our previous research<sup>27</sup> and from similar experiments repeated here for  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$ , we found that complete hydrolysis and equilibration of the headspace is complete in 3 h. After this time, the headspace can be sampled for analysis by GC/MS. Fluoroethane is a stable compound and was detected in the headspace up to three days after the derivatization. The chemical yield for derivatization, achieved using the experimental conditions described herein, was determined to be 8%. For this purpose, four fluoride standard solutions were prepared and subjected to the ethylation procedure. The

headspace was then purged with nitrogen to eliminate the fluoroethane and the remaining solutions were analyzed for the residual content of fluoride.

The purpose of this work was to demonstrate the performance of  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$  for derivatization of fluoride. However, one must be mindful that, much like  $\text{Et}_3\text{O}^+[\text{BF}_4]^-$ , triethyloxonium tetrachloroferrate is also able to ethylate other inorganic anions.<sup>27</sup>

### Figures of merit and applications

The determination of fluoride was undertaken in various liquid matrices using a standard additions calibration approach whereby the fluoroethane peak ( $m/z = 47$  Da signal) was integrated and linearly regressed against the mass of fluoride added. Headspace sampling and injection into the GC/MS was manually performed; no internal standards were used to correct for variations that may occur during these operations. This method was validated using IRMM CA408 rainwater certified reference material, yielding good agreement with the certified property value, as summarized in Table 1. Other matrices were also examined, including City of Ottawa drinking water, seawater reference material (NRC MOOS-2), and urine from a healthy volunteer. Results are based on the mean values of three independent measurements derived from four point (in addition to the unspiked sample) standard additions curves and the uncertainties were evaluated according to the ISO/GUM guidelines. For each measurement, the relation between the mass of fluoride added and the integrated signal was always linear and characterized by a coefficient of determination  $R^2 > 0.99$ . The mass concentration of fluoride determined in City of Ottawa drinking water,  $\gamma(\text{F}^-) = 0.72 \pm 0.06$  mg/L, is in agreement with the target level of 0.70 mg/L recommended by Health Canada and adopted by the City of Ottawa.<sup>35</sup>

The results for the other two samples were as follows:  $\gamma(\text{F}^-) = 0.59 \pm 0.07$  mg/L in urine and  $\gamma(\text{F}^-) = 1.39 \pm 0.09$  mg/L in north Atlantic water (MOOS-2). The fluoride content in MOOS-2 is also in good agreement with ion selective electrode measurements of ocean water of similar salinity.<sup>36</sup>

All samples yield three phases after derivatization with  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$ : (1) a precipitate which contains  $\text{Fe}(\text{OH})_3$  and part of the matrix, (2) a homogeneous aqueous phase, and (3) an upper gas phase (headspace) from which the fluoroethane is sampled. Derivatization allows separation of the analyte from the sample into the headspace and enables the realization of extremely clean chromatograms. Figure 2 shows the results from a urine sample; even with such a complex matrix, there are no interferences co-eluting with the analytical peak. The instrumental limit of detection obtained by processing calibration solutions is  $\gamma(\text{F}^-)_{\text{DL}} = 3.2 \mu\text{g/L}$  with a linear range up to 50 mg/L. The estimation of  $\gamma(\text{F}^-)_{\text{DL}}$  is based on the signal-to-noise ratio calculated from the standard deviation of the baseline in proximity to the analyte peak (*i.e.* detection limit is the concentration which produces a signal-to-noise-ratio of three). Standard solutions of  $\gamma(\text{F}^-) = 123 \mu\text{g/L}$  and  $531 \mu\text{g/L}$  give signal-to-noise ratios of 115 and 492, respectively.

### Interferences

Fluoride forms strong complexes with many metal cations, such as  $\text{Al}(\text{III})$ , and  $\text{Fe}(\text{III})$ . These interferences are common to any method of determination of fluoride. Therefore, the method of standard additions should be used to overcome such matrix effects.<sup>36</sup> Interferences arising from the complexation of fluoride reduce the analytical signal and deteriorate the performance of analytical methods. Therefore, the effect of the presence of large amounts of various metal cations on the analytical response was evaluated. Table 2 summarizes the interference arising from the presence of 10 mM (240–650 mg/L) levels of several cations added to standard solutions containing 0.05 mM fluoride. The 200-fold excess of these potential interferences over the analyte was chosen in order to show the robustness of the proposed method in coping with the interference of metal cations. Signal suppression is observed in the presence of  $\text{Mg}(\text{II})$ ,  $\text{Ca}(\text{II})$ ,  $\text{Fe}(\text{III})$ , and  $\text{Al}(\text{III})$ . The latter exhibits the most severe suppression and contributes to a ten-fold decrease in the analytical signal. Negligible effects were evident with  $\text{Zn}(\text{II})$ , and  $\text{Cu}(\text{II})$ . The

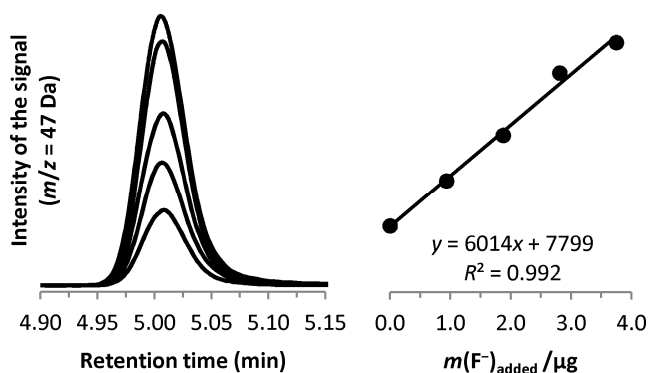
alkaline condition induced by pretreatment of the sample with ammonia results in precipitation of many metal cations as hydroxides, thus significantly reducing their ability to complex fluoride.

**Table 1.** Determination of fluoride in IRMM CA408 rainwater certified reference material.<sup>a</sup>

| run                     | $\gamma(\text{F}^-)/(\text{mg/L})^b$ |
|-------------------------|--------------------------------------|
| 1                       | $0.186 \pm 0.034$                    |
| 2                       | $0.196 \pm 0.020$                    |
| 3                       | $0.195 \pm 0.017$                    |
| 4                       | $0.199 \pm 0.011$                    |
| <b>mean</b>             | <b><math>0.194 \pm 0.012</math></b>  |
| <b><math>u_r</math></b> | <b>6.5%</b>                          |

<sup>a</sup>Certified property value:  $\gamma(\text{F}^-) = 0.194 \pm 0.008$  mg/L.

<sup>b</sup>Uncertainty of each standard additions experiment was evaluated according to ISO/GUM guidelines. All uncertainties are reported here as expanded uncertainties with coverage factor  $k = 1$ .



**Figure 2.** Analytical peaks for fluoroethane (at  $m/z = 47$  Da) and the resulting standard additions calibration plot derived from a sample of incrementally spiked urine.

**Table 2.** Interference effect arising from the presence of 10 mM metal ion in a standard solution of 0.05 mM fluoride.

| Interference | $S/S_0^{(a)}$   |
|--------------|-----------------|
| None         | $1.00 \pm 0.07$ |
| Al(III)      | $0.11 \pm 0.09$ |
| Fe(III)      | $0.62 \pm 0.07$ |
| Ca(II)       | $0.83 \pm 0.03$ |
| Mg(II)       | $0.32 \pm 0.02$ |
| Zn(II)       | $0.97 \pm 0.06$ |
| Cu(II)       | $1.01 \pm 0.06$ |

<sup>(a)</sup>  $S/S_0$  is the ratio between the analytical signal from fluoride in the presence of interference (S) to that generated without interference ( $S_0$ ). Three independent measurements were performed.

## CONCLUSIONS

Triethyloxonium tetrachloroferrate(III) was successfully employed for derivatization of fluoride ion in aqueous solutions to produce stable volatile fluoroethane, which is amenable to analysis by GC/MS. Although it is a lower throughput approach compared to ion selective electrode methods, this novel ethylation chemistry coupled with GC/MS provides better selectivity and specificity. With respect to other GC/MS approaches, this method offers a comparable or better detection limit, and it is considerably safer to use than silylation or alkylation with  $\text{F}_5\text{BzBr}$  because  $\text{Et}_3\text{O}^+[\text{FeCl}_4]^-$  is a water soluble salt which undergoes complete hydrolysis in a few hours. Additionally, it is not a volatile liquid such as  $\text{Me}_3\text{SiCl}$  and the oxonium alkylation proceeds in aqueous media at room temperature which adds to the speed and convenience of the method. Further improvement to the analytical figures of merit appears possible by employing an internal standard. Bromide and iodide ions should serve as ideal internal standards since they undergo the same derivatization chemistry as fluoride.

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