

Analysis of Fluoride in Drinking Water in the Presence of Interfering Metal Ions Such as Iron and Aluminum

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ABSTRACT

Fluoride is typically added to drinking water to reduce tooth decay. To be effective, the level of fluoride in drinking water needs to be strictly controlled. To protect children from dental fluorosis, the U.S. EPA has set an enforceable drinking water standard for fluoride of 4 mg/L and a secondary fluoride standard of 2 mg/L.

In typical drinking waters, the analysis of fluoride is accomplished by Ion Selective Electrodes (ISE) or by Ion Chromatography (IC). However, in some drinking water samples there is a high level of iron or aluminum which has been added during the water treatment process. These metal ions can form a complex with fluoride and complicate the analysis. In order to release fluoride, complexing reagents, such as 1, 2-cyclohexanedinitrilo-tetraacetic acid (CDTA), are typically added to bind to the aluminum or iron, thereby facilitating the detection of fluoride by ISE. In this poster, we examine the performance of suppressed IC for fluoride analysis in the presence of interfering metal ions, such as iron or aluminum without added complexing reagents. We also compare the results between the IC and ISE methods and show examples of fluoride analysis in a variety of drinking water and simulated drinking water samples.

INTRODUCTION

Fluoride occurs naturally in all types of water. Typically, surface waters and seawaters have low concentration of fluoride while groundwater may contain high levels of fluoride as it may be exposed to many inorganic fluoride-containing minerals. Fluoride salts are also frequently encountered in many industrial applications. For example, aluminum fluoride is used as an additive in the production of aluminum by electrolysis. Also, the production of phosphate fertilizer from rock phosphates will release fluoride as a byproduct. The removed and purified fluoride (for example, hexafluorosilicate) is a source of fluoride in municipal water fluoridation.

FLUORIDE HEALTH BENEFITS AND ISSUES

Low levels of fluoride can help prevent dental cavities. However, higher levels of fluoride can induce dental fluorosis, which is the brown staining and/or pitting of permanent teeth. This occurs only in developing teeth before they erupt from gums. Thus, children under nine should not drink water that has more than 2 mg/L of fluoride.

Long-term exposure to high levels of fluoride can also lead to skeletal fluorosis. The fluoride level in drinking waters needs to be monitored and strictly controlled.

FLUORIDE REGULATION IN DRINKING WATER

Currently, the US EPA has set an enforceable maximum contaminant level (MCL) for fluoride at 4 mg/L, with a maximum contaminant level goal (MCLG) at 4 mg/L under National Primary Drinking Water Regulations (NPDWRs). Also, the US EPA has set a secondary MCL for fluoride at 2 mg/L, with a MCLG at 2 mg/L under National Secondary Drinking Water Regulations (NSDWRs). The World Health Organization (WHO) also sets a guideline value of 1.5 mg/L for fluoride in drinking waters.

Table 1. Current Methods for Fluoride Analysis

| Techniques | Published Methods |
|-------------------------|-----------------------------|
| Ion Chromatography | EPA 300.00, 300.1 |
| | OSW 9056A |
| | ASTM D4327-91 |
| | Standard Methods 4110B |
| Ion-Selective Electrode | EPA 340.2 |
| | OSW 9214 |
| | ASTM D1179-93B |
| | Standard Methods 4500F-C |
| Colorimetry | EPA Method 340.1, 340.3 |
| | Standard Methods 4500F-D, E |

ION-SELECTIVE ELECTRODE (ISE) METHOD

The Fluoride ISE method was invented by Frant and Ross in 1968. This method utilizes a fluoride selective membrane, which is typically a lanthanum fluoride crystal. The fluoride activity is measured according to the following equation.

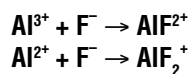
$$E = E_0 - RT/F \ln [F^-] \text{ (Fluoride activity)}$$

The method is sensitive to solution pH. At low pH, fluoride can form hydrofluoric acid, which lowers the measurement. At high pH, hydroxide can also respond to the ISE and increase the measurement.

A Total Ionic Strength Adjustment Buffer (TISAB) solution is typically added to the samples to adjust the solution pH to an optimum value of 5.0 ~ 5.5. The relatively high ionic strength from the TISAB can also minimize the liquid junction potentials and provide constant ionic strength for samples and standards.

ISE - INTERFERENCES

Fluoride can form stable complexes with high valence cations, such as aluminum, iron, and magnesium, which can lead to lower response



To release fluoride from complexes, decomplexing reagents are used, including:

- Citrate
- CDTA
- Tiron (pyrocatechol 3,5 di-sodium sulfonate)
- Tris
- Mannitol
- Triethanolamine
- Salicylate

Table 2. Fluoride Response in the Presence of Metal with CDTA as the Decomplexing Reagent Using the ISE Method

| F (ppm) | Al (ppm) | Fe (ppm) | Amount (ppm) | % REC |
|---------|----------|----------|--------------|-------|
| 1 | 1 | | 1.04 | 104 |
| 1 | 5 | | 0.973 | 97.3 |
| 1 | 25 | | 0.703 | 70.3 |
| 1 | 50 | | 0.515 | 51.5 |
| 1 | | 1 | 1.04 | 104 |
| 1 | | 5 | 1.02 | 102 |
| 1 | | 25 | 0.989 | 98.9 |
| 1 | | 50 | 1.00 | 100 |
| 1 | 1 | 1 | 1.04 | 104 |
| 1 | 5 | 5 | 0.966 | 96.6 |
| 1 | 25 | 25 | 0.697 | 69.7 |

Table 2 shows the response of fluoride using the ISE method. At high levels of aluminum, the fluoride response decreases significantly. CDTA is not able to decomplex fluoride completely from aluminum.

Table 3. Current IC Method for Fluoride Analysis

| U.S. EPA Method | Analytical Technique | Analytical Column | Flow Rate (mL/min) | Loop Size (μL) | Detection Limit (mg/L) |
|-----------------|---|--------------------|--------------------|----------------|------------------------|
| 300.0 (A) | IC with Suppressed Conductivity Detection | IonPac® AS4A 4 mm | 2.0 | 50 | 0.010 |
| 300.1 (A) | IC with Suppressed Conductivity Detection | IonPac AS9-HC 2 mm | 0.40 | 10 | 0.009 |

Table 3 shows the current EPA methods for fluoride analysis. Both EPA methods utilize carbonate/bicarbonate eluents. A hydroxide eluent can also be used for this application.

WHY USE HYDROXIDE ELUENT?

The suppression product is water, thereby providing the lowest possible background conductivity. This results in lower baseline noise, improved detection limits, and wider linear range. Additionally, the hydroxide eluent can be conveniently generated online to further enhance precision, automation, and reduce downtime.

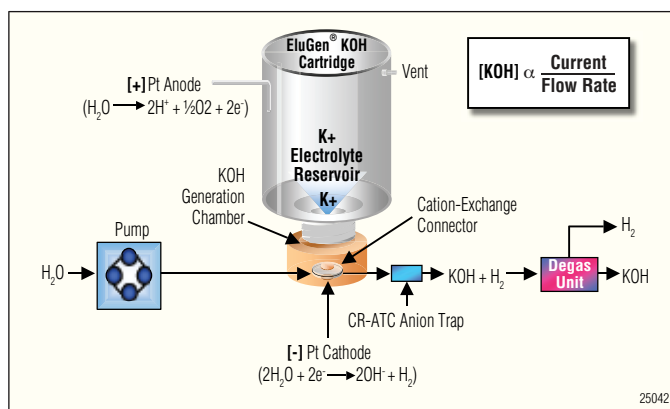


Figure 1. Hydroxide eluent generation for anion analysis.

Table 4. Column Characteristics

| | IonPac AS4A | IonPac AS14 | IonPac AS9-HC | IonPac AS18 |
|----------------------------------|-----------------------------|---------------------------|-----------------------------|-----------------------------|
| Dimension | 4 × 250 mm | 4 × 250 mm | 4 × 250 mm | 4 × 250 mm |
| Particle Diameter (μm) | 15 | 9 | 9 | 7.5 |
| Latex Diameter (nm) | 180 | Grafted | 90 | 65 |
| Column Capacity (μ equiv/column) | 20 | 65 | 190 | 285 |
| Functional Group | Alkanol Quaternary Ammonium | Alkyl Quaternary Ammonium | Alkanol Quaternary Ammonium | Alkanol Quaternary Ammonium |
| Hydrophobicity | Medium Low | Medium High | Medium Low | Medium Low |

Table 4 shows the column characteristics of various IonPac columns. A hydroxide-selective IonPac AS18 column is used for fluoride analysis.

2 Analysis of Fluoride in Drinking Water in the Presence of Interfering Metal Ions Such as Iron and Aluminum

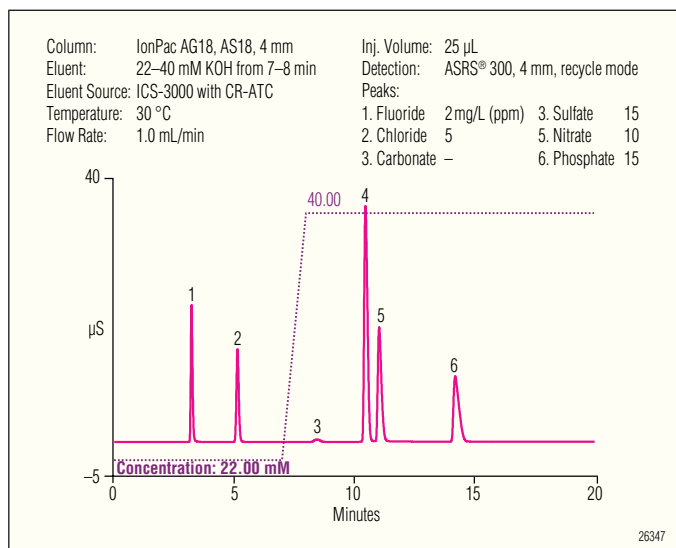


Figure 2. Direct IC analysis using the IonPac AS18 column.

Figure 2 shows the analysis of five common inorganic anions with an AS18 column. All five analytes were well-resolved.

| Table 5. IC Performance Using IonPac AS18 Column | | | | | |
|--|--------------|-----------------------------|--------------------------------|--------------------|----------------------|
| Anion | Range (mg/L) | Linearity (r ²) | Calculated MDL (µg/L) | Rt Precision (RSD) | Area Precision (RSD) |
| Fluoride | 0.1–100 | 0.9991 | 2.6 | 0.13% | 0.27% |
| Chloride | 0.2–200 | 0.9999 | 2.4 | 0.09% | 0.19% |
| Nitrite-N | 0.1–100 | 0.9992 | 1.5 (4.9 as NO ₂) | 0.06% | 0.25% |
| Bromide | 0.1–100 | 0.9999 | 5.6 | <0.05 | 0.73% |
| Nitrate-N | 0.1–100 | 0.9999 | 1.7 (7.3 as NO ₃) | <0.05% | 0.63% |
| <i>o</i> -Phosphate-P | 0.2–200 | 0.9998 | 6.2 (19.0 as PO ₄) | <0.05% | 0.19% |
| Sulfate | 0.2–200 | 0.9998 | 4.8 | <0.05% | 0.19% |

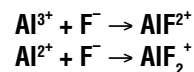
Table 5 lists the linearity, MDL, retention time, and area precision data using the Dionex ICS-2000 Reagent-Free™ IC system (RFIC™) with CR-ATC and a 25 µL injection. The MDL was obtained with seven replicates using MDL = $s t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$. The retention time and peak area RSD (Relative Standard Deviation) were also obtained with seven replicates.

| Table 6. Fluoride Response in the Presence of Metals | | | | |
|--|----------|----------|--------------|--------|
| F (ppm) | Al (ppm) | Fe (ppm) | Amount (ppm) | % REC |
| 1 | 1 | | 1.0374 | 103.74 |
| 1 | 5 | | 1.0425 | 104.25 |
| 1 | 25 | | 0.9796 | 97.96 |
| 1 | 50 | | 0.9053 | 90.53 |
| 1 | | 1 | 1.0216 | 102.16 |
| 1 | | 5 | 0.9873 | 98.73 |
| 1 | | 25 | 0.8953 | 89.53 |
| 1 | | 50 | 0.8894 | 88.94 |
| 1 | 1 | 1 | 1.0391 | 103.91 |
| 1 | 5 | 5 | 1.0313 | 103.13 |
| 1 | 25 | 25 | 0.9683 | 96.83 |

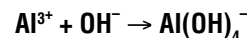
Table 6 shows the excellent fluoride recovery in the presence of interfering metal ions using the direct IC method with AS18 chemistry, even in the presence of 50 ppm aluminium and iron.

MECHANISM

- In the presence of aluminum, fluoride exists in both free and bound states:



- In the presence of hydroxide during the IC analysis, the hydroxide ion can act as a competing ion, binding to aluminum, freeing fluoride:



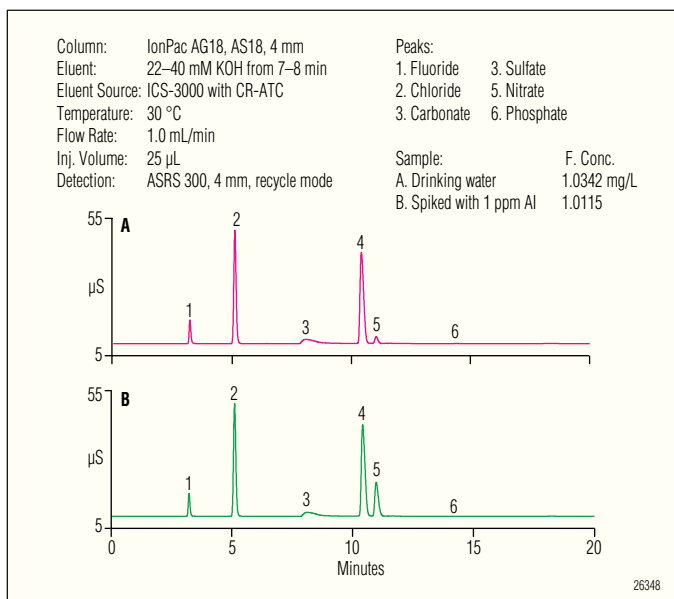


Figure 3. Drinking water analysis.

Figure 3 shows the analysis of a drinking water sample spiked with aluminum using the direct IC method. Excellent fluoride recovery was obtained.

CONCLUSION

- The fluoride level in drinking water can be monitored by several different methods.
- Although the ion-selective electrode method is a simple approach, it can not provide an accurate measurement for fluoride in the presence of metal cations.
- The addition of decomplexing reagents was found to alleviate the issue but was not adequate at all levels.
- A RFIC system using hydroxide eluent provides increased automation and ease-of-use:
 - Delivers good separation
 - Improved linearity and MDLs
 - Minimizes the interference from metal ions for fluoride analysis

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LPN 2339-01 9/09
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