

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ ﴿ وَقُلُ اعْمَلُوا فَسَيَرَى اللَّهُ عَمَلَكُ مُ وَمَرَسُولُهُ وَالْمُؤْمِنُونَ ﴾ صدقاللهالعليالعظيـــــ سومرةالتوبة الآية (105)





(شکر وتقدیر )

الحمد لله الأول قبل كل شيء والأخر بعد فناء كل شيء، والحمد لله الذي هدانا لهذا وما كنا لنهتدي لولا أن هدانا الله والصلاة والسلام على رسوله الكريم محمد (صلى الله عليه واله وسلم). واني أحمد الله تعالى على عظيم فضله الذي مكنني من إنهاء هذه الدراسة ووفقني لانجاز هذا الجهد العلمي داعى الله إن يكون علماً نافعاً خالصاً لوجهه تعالى.

من الحق والوفاء وأنا أنتهى من إعداد هذه الدراسة ، أن أتقدم بأسمى آيات الشكر والتقدير والامتنان إلى أستاذي الفاضل المحكتور حسن محصد لعيبيي، لجهوده العلمية القيمة ورعايته المخلصة لانجاز هذه الدراسة. وأرى من الوفاء أن أهدي شكري وتقديري إلى الأساتذة الأفاضل رئيس وأعضاء لجنة المناقشة لقبولهم مناقشة البحث.

ويلزمني الواجب أن ابدي خالص اعتناني وغرفاني بالبعيل إلى أساتذتي في كلية العلوم /جامعة القادسية / لما قدموا من مبصود وتوصيات دلت على دقة عملمو وكرو أخلاقمو وأتمنى لمو الموفقية والصحة الدانمة.

وشڪرا وعذيرا لڪل من نساء قلمي ولمرينسه قلبي وفڪري من أصدقائي ويزملائي وإخوتي أينما كانوا . . .

## Abstract

The concentrations of chloride, fluoride, and sulfate were determined in various water samples by ion chromatography. It was determined that water from Prey's Pond, the Red River, Moorhead tap, Fargo tap and Concordia College drinking water contained high levels of sulfate, with Prey's Pond containing the highest concentration of sulfate. Moorhead tap water had the highest fluoride and chloride concentrations.

determination of common inos (anion and cation) in water samples was developed. For comparison, selected samples of tap water, underground water, bottled mineral water and filtered tap water were collected and determined from Talkha and some villages, Dakahlia, Egypt. Ten ions of each anion and cation (fluoride, chloride, bromide, nitrate, sulphate, sodium, ammonium, magnesium, potassium, and calcium) were separated and analyzed, respectively. An isocratic elution with 4.5mmol/L Na2CO3, 1.0 mmol/L NaHCO3 and 42 mmol/L methanesulfonic acid (MSA), IonPac AS22 and CS16 as the separation column and DS6 heated conductivity detector was used. The validation of the analytical method was studied in terms of linearity, sensitivity and accuracy. The linearity was between 0.9922 and 0.9992. And the detection limits ranged from  $0.4\mu g/L$  to  $72\mu g/L$  (S/N = 3) and satisfactory repeatability (RSD < 2.82%, n = 6). The recoveries were between 91.3% and 116.6%. All water samples were within the safety and acceptable levels of the World Health Organization (WHO, 2006) guidelines. Out of the samples of drinking water, only underground water had the slightly higher levels.

# Introduction

Water is the most important substance for plant and animal life. However, water in nature is rarely pure and typically contains a wide range of elements and compounds. Common anions found at high concentrations in water systems around the Fargo-Moorhead area are chloride, fluoride, and sulfate.

The EPA's National Secondary Drinking Water Regulations were created in order to monitor and control the levels of certain substances in water throughout the United States. They recommend, but do not require, drinking water to contain less than 250 ppm chloride, 2 ppm fluoride, and 250 ppm sulfate.1

Chloride and fluoride are very common in water systems as they are added to drinking water for various health and sanitary purposes. However, chloride and fluoride levels can be increased by contamination of fertilizers, road salt, and industrial pollution as well as human and animal waste.2 The contaminants can cause dramatic increases in chloride and fluoride concentrations, which should be closely monitored.

The Red River Valley water systems typically have relatively high sulfate concentrations. As part of the Safe Drinking Water Act, sulfate is expected to be regulated as high sulfate concentrations can contribute to illness, such as diarrhea, especially for infants, elderly people, and individuals who may be travelling or are not accustomed to high levels of sulfate.3

Ion chromatography is a popular method of analysis for determining concentrations of ions and as well as polar molecules based on charges in liquid samples. It is a common system used for quality control and water analysis as it can be used for a wide variety of analytes. This experiment uses ion chromatography because of its ability to determine the concentrations of multiple chemical species simultaneously in order to determine the levels of fluoride, chloride and sulfate in water samples obtained from the Fargo-Moorhead area.

determination of common inorganic anions in drinking water matrices. The IonPac AS14A provides greater speed and efficiency, ruggedness equivalent to the AS4A-SC column, improved separation of fluoride from the void volume (water dip), and better overall separation selectivity. The AES is a continuously electrolytically regenerated suppressor based on the MonoDisc<sup>™</sup> suppression technology. The Atlas electrolytic suppressor offers lower baseline noise and improved ruggedness and reliability. The analytical throughput, potential interferences, linear range, method detection limits, system stability, and analyte recoveries obtained using the AS14A column with the Atlas suppressor for drinking water are described in this Application Note .lon chromatography (IC) is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on their interaction with the particular resin. Its greatest utility is for analysis of anions. It is also used in the analysis of cations and biochemical species such as amino acids and proteins. The column packings for ion chromatography consist of ion exchange resins bonded to inert polymeric particles (typically 10 µm diameter). The DX-300 used in this experiment contains an anion exchange column, a ã Dionex (www.dionex.com) IonPacâ AS9-HC (2-mm) Analytical Column. Cation exchange is used to illustrate the general theory of IC in this introduction. It will be up to the student to formulate the general theory for anion exchange.

# Theory

The determination of common inorganic anions in drinking water is one of the most important applications of ion chromatography (IC) worldwide. The National Primary Drinking Water Standards in the United States specify a Maximum Contaminant Level (MCL) for a number of inorganic anions, including fluoride, nitrite, and nitrate. The MCLs are specified to minimize potential health effects arising from the ingestion of these anions in drinking water.

High levels of fluoride cause skeletal and dental fluorosis, and nitrite and nitrate can cause methemoglobulinemia, which can be fatal to infants. Other common anions,

such as chloride and sulfate, are considered secondary contaminants. The National Secondary Drinking Water Standards in the U.S. are guidelines regarding taste, odor, color, and certain aesthetic characteristics. Although these guidelines are not federally enforced, they are recommended to all states as reasonable goals and many states adopt their own regulations governing these contaminants.

This application note describes the determination of inorganic anions in drinking water and other environmental waters using conditions that are consistent with those in U.S. EPA Method 300.0.3 The use of an optional column, the Thermo Scientific Dionex<sup>™</sup> IonPac<sup>™</sup> AS14 column,

is also discussed.

# Experimental

Standard Solution Preparation Standard solutions were created using 1000-ppm chloride (Metrohm-Peak, Inc), 1000-ppm fluoride (Fluka) and 1000-ppm sulfate (SPEX CertiPrep) standards. A 5-mL aliquot of each standard was diluted with distilled water to a volume of 500 mL to make a 10-ppm solution. The 10-ppm solution was then diluted to 2, 4, 6 and 8 ppm solutions by pipetting 20, 40, 60, and 80 mL into 100-mL volumetric flasks respectively and filling to volume with distilled water.

# **Eluent Preparation**

Eluent was prepared by dissolving approximately 339 mg anhydrous sodium carbonate and approximately 84 mg sodium hydrogen carbonate in distilled water. The solution was diluted to 1.00 L with distilled water in a volumetric flask and was filtered with a Millipore 0.45-µm glass frit filtration system coupled with a 0.20-µm nylon filtration membrane before use.

#### **Sample Preparation**

Water samples were obtained from various locations including Prexy's Pond, the Red River, Moorhead tap water, Fargo tap water, and a drinking fountain at Concordia College. Each sample was diluted by pipetting 5 mL into a 50-mL volumetric flask and filling to volume with distilled water. This solution was then diluted once more by pipetting 10 mL of each sample into a 50-mL volumetric flask and diluting with distilled water. Samples were analyzed at the original concentration as well as the final, 1:50, concentration. The chloride and fluoride levels were easily determined from the original sample; however the sulfate levels were significantly higher and were determined using the 1:50 diluted water samples.

### Instrument

A Metrohm ion chromatography system was used in conjunction with a conductivity detector. The column used for separation was a Metrosep A Supp 5-100 column, at 4.0 x 100 mm with particle size 5.0  $\mu$ m. Analysis was carried out with a flow rate of 0.70 mL per min at 35.0°C. The injection loop volume was 25.0  $\mu$ L.

### **Results and discussion**

#### **Calibration Curves**

Each peak was determined to be representative of a specific anion at varied retention times due to the differences in charge and mass of each species. A fluoride peak Concordia College Journal of Analytical Chemistry 3 (2012), 24-28 26 was detected around 2.99 min, a chloride peak was seen around 4.06 min, and the sulfate peak was visible around 10.14 min (Fig. 1). Each peak was monitored at the respected retention time as concentration varied for each standard solution. These values were used to generate calibration curves for each species (Fig. 2) which were used to determine the concentration of each anion in the water samples. The correlation coefficients for fluoride, chloride, and sulfate were 0.9927, 0.9971, and 0.9996 respectively.



Figure 1. Sample chromatogram of mixed standard with fluoride concentration of 2 ppm, chloride concentration of 4 ppm, and sulfate concentration of 8 ppm.



Figure 2. Calibration curves of standard concentrations. Fluoride concentration vs. peak area around 2.99 min. Chloride concentration vs. peak area around 4.06 min. Sulfate concentration vs. peak area around 10.14

# Analysis of Water Samples

In each of the five water samples, significant peaks appeared near 2.99, 4.06, and 10.14 min, correlating to the retention times of fluoride, chloride, and suflate as determined by the standard calibration curves (Fig. 3). In a blank sample of only distilled water, these anions were not present at any detectable level.





Figure 3. Chromatograms of water samples obtained from a.) Prexy's Pond. b.) Red River c.) Moorhead tap d.) Fargo tap e.) Concordia College drinking fountain and f.) Distilled water.

The data collected from each chromatogram in two separate trials was used to calculate concentrations of the three different anions in each water sample. The average concentration was determined and standard deviations were calculated (Table 1).

Table 1. Measured concentrations of anions in water samples. (Mear	า
± standard deviation)	

Water System	[F-] (ppm)	[Cl-] (ppm)	[SO4-] (ppm)	Water System	[F-] (ppm)
Drovy's Dond	0.95	24 79	204.8	Drovy's Dond	0.05
Trexy ST ond	(±.04)	(±.30)	(±1.9)	i rexy s r onu	(±.04)
Red River	0.16 (±0)	21.24 (±.21)	181.2 (±2.7)	Red River	0.16 (±0)
Concordia College	1.285 (±.078)	26.70 (±.51)	202.7 (±2.4)	Concordia College	1.285 (±.078)

### Conclusions

This experiment was used to determine the concentrations of various anions in samples obtained from multiple water systems using ion chromatography. Moorhead tap water was determined to have the highest concentration of fluoride ( $1.295 \pm 0.092$  ppm) and chloride ( $27.87 \pm 0.55$ ), while Prexy's Pond was found to contain the highest concentration of sulfate ( $204.75 \pm 1.91$ ). It was determined that all water samples from the Fargo- Moorhead area contained fluoride concentrations under 1.5 ppm, chloride concentrations under 30 ppm and sulfate concentrations around 200 ppm. All concentrations were found to be below the levels that are suggested by the Safe Water Act.

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