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Measurement of Ammonium by Ion Chromatography in High Sodium Concentration

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ABSTRACT

Chemical analysis of Antarctic ice cores provides valuable information on the history and dynamics of the atmosphere environment. The ice core samples contain trace amounts of ammonium, sodium, and other ionic chemical species, which are usually, measured using ion chromatography. High concentrations of sodium may interfere with the accurate and precise measurement of ammonium, due to insufficient resolution of their chromatographic peaks. The extent of the interference is investigated in this project by quantitative determination of the ammonium concentration in solutions of various ammonium and sodium concentrations. A criterion of 20% relative error of measured ammonium concentration is used to determine the threshold of sodium concentration that results from unacceptable resolution of ammonium and sodium peaks. The results of this investigation can be incorporated in the routine analysis of ice cores using ion chromatography. Keywords: peak resolution, ion chromatography

INTRODUCTION

Snow in polar ice sheets is a valuable archive of the atmosphere and of atmospheric environment. Measurement of the chemical composition of snow and ice, having accumulated over long periods of time, gives the history of ammonium and other ions. Ammonium measurement is used as a tracer of biomass burning and forest fires.

Ion measurements can be made using ion chromatography (1). In the 1960s and early 1970s, wet chemical methods and electroanalysis were used to measure low molecular weight inorganic anion and cations. The development of improved stationary phases and detection methods in 1975 led to the development of modern ion chromatography (2).

Ion chromatography is used to separate multiple ions in a sample and to determine their concentrations. The most common form of separation is ion-exchange chromatography, in which an anion exchange column separates anions, while cations are separated by a cation exchange column (3). Ion

exchange chromatography consists of two phases: mobile and stationary phase. Analyte ions are separated by differences in their strength of electrostatic attraction for functional groups of the stationary phase. The relationship of electrostatic attraction and partitioning between the two phases dictates the time it takes for the analyte ion to reach the detector. This period of time is known as retention time. Stronger electrostatic attraction results in more time spent in the stationary phase and therefore longer retention times of analytes. Ion chromatography identification is achieved by comparison of retention times of the analyte in sample and in standard (4). Chromatographic variables that affect retention time include eluent strength, flow rate and temperature. Due to analysis constraints such as time, peaks can show some overlap, which results in interference with the determination of analytes present in solutions. For example, in snow and ice analysis, sodium can interfere with the determination of ammonium concentrations. Typically, to obtain sufficient peak resolution, several factors can be adjusted. The maximum retention time can be increased by decreasing the flow rate or the eluent concentration. However, those adjustments were not applicable for this specific study since a maximum of 3.9-minute chromatographic run time, determined from an analytical technique involving Antarctic ice cores, was required (1). Even under optimized conditions, the sodium and ammonium peaks overlap (1). Since the sodium concentrations in Antarctica snow are typically much larger than ammonium concentrations (about 50 ppb and 1 ppb, respectively), the measured ammonium concentrations contained inaccuracies due to sodium peak overlap.

The objective of this research was to determine what concentrations of sodium will and will not interfere with accurate ammonium concentration measurement.

METHOD

The instrument used was a Dionex DX600 ion chromatograph equipped with a CS12A column with suppressed conductivity detection. A Dionex AS40 auto-sampler held 5 mL plastic vials containing the sample solutions, which were then loaded onto a 500- μ L sample injection loop that was used to achieve large analyte peaks for low concentrations of cations in Antarctic snow and ice samples. The chromatographic conditions used for this experiment consisted of a dilute H₂SO₄ eluent solution with a flow rate of 0.70 mL/min and a self-regenerating suppressor (SRS) current reading of 50 mA. The same column was used throughout the experiment. All glassware was cleaned with deionized water multiple times while wearing latex gloves to prevent contamination. Stock solutions (1000 ppm) of sodium and of ammonium were used to make an intermediate stock solution of 100 ppb for each ion. The intermediate stock solution was further diluted to generate each concentration combinations found in Table 1.

Table 1. Concentration combinations of test samples. The ammonium concentration in each row is the same, as indicated in Column 1.

Ammonium Conc. (ppb)	Sodium Conc. (ppb)	Sodium Conc. (ppb)	Sodium Conc. (ppb)	Sodium Conc. (ppb)	Sodium Conc. (ppb)	Sodium Conc. (ppb)	Sodium Conc. (ppb)
1	0	5	10	20	30	40	50
3	0	5	10	20	30	40	50
5	0	5	10	20	30	40	50
10	0	5	10	20	30	40	50
15	0	5	10	20	30	40	50

Samples containing only ammonium (Column 2 in Table 1) were used to create an ammonium calibration curve. Each sample combination was tested five times. As a precaution, fresh standard solutions were made daily and were tested at the beginning and end of each day to monitor for any concentration change that may have occurred.

RESULTS AND DISCUSSION

The problem of sodium interference of ammonium concentration was evaluated thoroughly by ion chromatography. Ammonium measurements encounter interference in the presence of sodium as shown in Figure 1. The Dionex chromatography software used to obtain the size of the peaks overestimates the ammonium peak by using a single baseline for both the sodium peak and the ammonium peak, due to the overlap or incomplete separation of the two peaks (Figure 1). The long tail of the large sodium peak contributes to the measured size of the ammonium peak. This results in measured ammonium concentrations that may be higher than the actual concentrations.

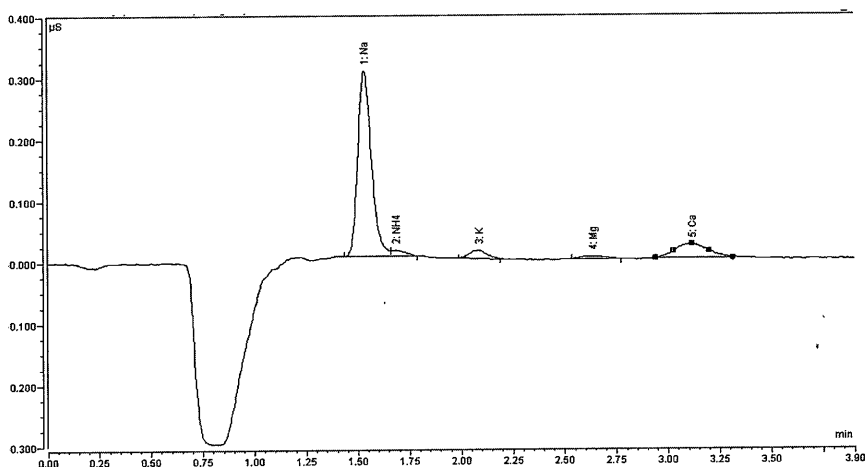


Figure 1. Chromatogram showing unresolved ammonium and sodium peaks.

To analyze the data, the ammonium concentrations determined using ion chromatography were plotted against sodium concentrations. Figure 2 shows the average measured concentrations of 5 ppb prepared ammonium solutions as a function of sodium concentration. The figure shows that, initially, the measurement of ammonium concentration is affected by sodium only slightly. However, as the sodium concentration increases, the measured ammonium concentration deviates significantly from the prepared 5 ppb concentration.

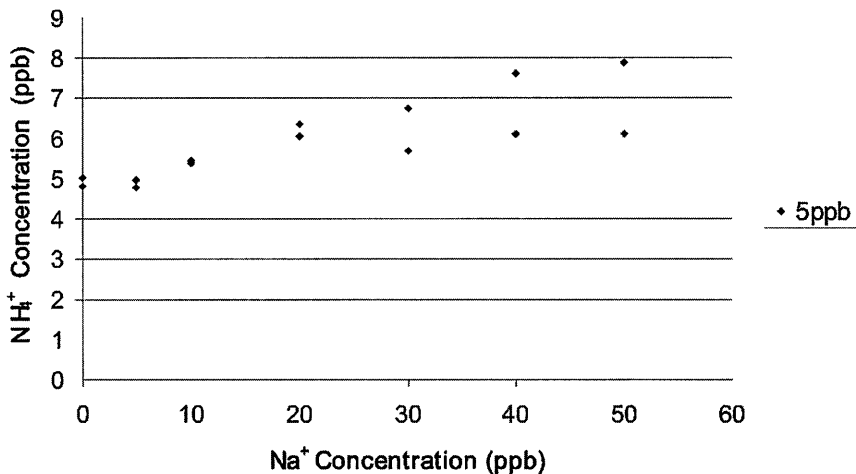


Figure 2. Two trials were graphed with the average measured ammonium value of each prepared ammonium concentration versus sodium concentration. When sodium concentration exceeds 10 ppb, interferences by sodium concentration are evident on ammonium concentrations made at 5ppb.

Several trials were made in which a series of solutions of a prepared ammonium concentration and increasing sodium concentrations were chromatographed and ammonium concentrations measured (Figure 2 shows only 2 replicate series at 5 ppb prepared ammonium concentration). Replicate measured ammonium concentrations were averaged, after a Grubbs test (5) was used to eliminate outliers. Subsequently, the average measured ammonium concentrations were graphed against sodium concentration in a fashion similar to that shown in Figure 2. A second-degree polynomial trendline was used to fit the data points. This procedure was applied to the series of sample solutions for all ammonium concentrations listed in Table 1. All of the trendlines are shown in Figure 3.

Typically, measurements of ion concentrations of polar snow and ice are acceptable with a 10% error (1). In this study, it is assumed that 20% error is acceptable for measurement of extremely low ammonium concentrations. Multiplying each prepared ammonium concentration by 20% and adding that value to the prepared ammonium concentration yields an acceptable maximum measured ammonium concentration. The sodium concentration that causes the prepared ammonium concentration to increase to this measured ammonium concentration can be obtained by solving for x in the trendline equation. For example, at 3 ppb prepared ammonium concentration, the acceptable maximum measured concentration is 3.6 ppb. Substituting 3.6 for y in the second order polynomial equation of $y = -0.0016x^2 + 0.1214x + 3$ and solving the equation

yields a sodium concentration (x variable) of 4.8 ppb. This data point of 3.6 ppb measured ammonium and 4.8 ppb sodium is indicated by the triangle on the 3 ppb line in Figure 3. Such a data point can be obtained for each of the trendlines (or prepared ammonium concentrations) in Figure 3.

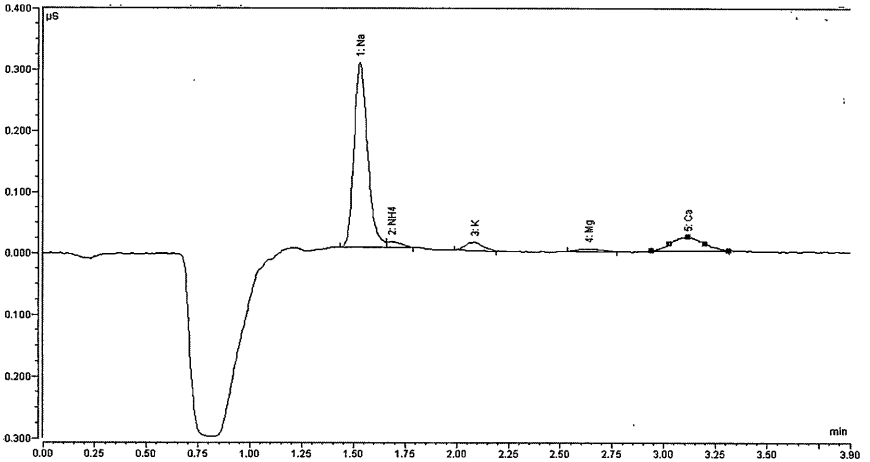


Figure 3. Measured ammonium concentrations versus sodium concentrations. The linear fit line represents 20% error of measured ammonium concentration.

A linear fit by least squares regression to all triangles in Figure 3 produces a line (20% Error line) that separates measured ammonium concentrations into two categories: acceptable and unacceptable. To the upper-left of the line, measured ammonium concentrations are acceptable because the error or deviation from the true ammonium concentration is less than 20% of the true value. Combinations of ammonium and sodium concentrations to the lower-right of the line result in measured ammonium concentrations to be more than 20% of the true concentration. An example of using Figure 3 is that, when measuring 10 ppb ammonium concentration in a snow sample, one finds that when sodium concentration is 31 ppb (circle in Figure 3), then the error of measured ammonium concentration is 20% of the true or real concentration and that the measured result is acceptable. However, if the sodium concentration in snow is above 31 ppb, then the error is too great and the measured ammonium concentration is not acceptable.

CONCLUSION

This study found the sodium ion concentration threshold that will yield ammonium concentration with 20% or more error of the true ammonium concentration, under the specific condition of an ion chromatography run time of 3.9 minutes. This threshold depends on the ammonium concentration being measured and increases as the measured ammonium concentration increases, according to the straight line in Figure 3. This method of determining the threshold of interference may be applied to other ion pairs under similar chromatographic conditions. Therefore, this method can be incorporated into future ice core chemistry research projects.

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