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**Ion Chromatography: Sample Analysis of
Ammonium Nitrate and Other Cations and
Anions**

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RESEARCH AND TECHNOLOGY DIRECTORATE

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PREFACE

The work described in this report was started in October 2016 and completed in August 2018. At the time this work was performed, the U.S. Army Combat Capabilities Development Command Chemical Biological Center (CCDC CBC) was known as the U.S. Army Edgewood Chemical Biological Center (ECBC).

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ION CHROMATOGRAPHY: SAMPLE ANALYSIS OF AMMONIUM NITRATE AND OTHER CATIONS AND ANIONS

1. INTRODUCTION

The U.S. Army Edgewood Chemical Biological Forensic Analytical Center (EC/B FAC), which is part of the organization now known as the U.S. Army Combat Capabilities Development Command Chemical Biological Center (CCDC CBC [Aberdeen Proving Ground, MD]), has developed an analytical method for investigating samples using ion chromatography (IC). Specifically, this method is used to detect and determine the concentration of the water soluble anionic components of inorganic explosives in solid bulk explosive samples by IC. This method is used to specifically quantitate the concentration of various anions that include fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), bromide (Br^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), and phosphate (PO_4^{3-}) in aqueous matrices, which include water extracts of a variety of explosive matrices. The method also quantitates the concentration of various cations that include calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonium (NH_4^+), sodium (Na^+), lithium (Li^+), and potassium (K^+) in aqueous matrices including water extracts of a variety of explosive matrices.

2. BACKGROUND

A central mission of the EC/B FAC is to develop and validate quantitative analytical methods, with a focus on those methods that address elemental analysis of materials. The EC/B FAC forensic abilities were originally developed to support United States obligations under the Chemical Weapons Convention, whereby the United States was required to procure sampling and analysis expertise to verify treaty compliance. The EC/B FAC is accredited to a standard produced by the International Organization for Standardization (ISO) and the International Electrotechnical Commission (IEC), ISO/IEC 17025, which refers to laboratory operations and quality control.¹ By demonstrating high standards in chemical and biological agent detection and analysis, the EC/B FAC maintains an elite status in international proficiency testing sponsored by the Organisation for the Prohibition of Chemical Weapons (The Hague, Netherlands).

Protecting soldiers in the field is of vital importance. One aspect of this protection is identification of the chemical composition and quantity of improvised explosive devices (IEDs). Ammonium nitrate is the nitrate salt of the ammonium cation. It is a white crystalline solid that is highly soluble in water. Ammonium nitrate is common in the agriculture industry as a fertilizer; however, this common fertilizer has gained popular usage as an explosive. As an explosive, it is easy to use and readily available. Rebels are using ammonium nitrate in IEDs daily, especially during the Afghanistan conflict and even continuing to the most recent Syrian conflict. Other combinations of inorganic salts, such as potassium nitrate, sodium chlorate, potassium perchlorate, sodium chlorate, and ammonium perchlorate, have also been linked to IEDs. Distinguishing between the different combinations of these anions and cations is useful for piecing together the forensic attribution of different explosives. IC provides a method for

simultaneously detecting and quantifying anions and cations to provide immediate information on the identity of the potential explosive.

The Dionex ICS-2100 system (Thermo Scientific Dionex; Sunnyvale, CA) is the first reagent-free IC (RFIC) system with electrolytic sample preparation and eluent generation capabilities that are designed to perform all types of electrolytically generated isocratic and gradient IC separations using conductivity detection.² The samples were prepared using NERL-grade water (Thermo Scientific) and commercially available standards.

3. MATERIALS AND METHODS

3.1 Materials

Laboratory-grade chemicals from any supplier are appropriate for this procedure. The following chemicals were used for the development and validation of this method:

- NERL reagent-grade water (or better) (Thermo Fisher Scientific [Waltham, MA] 9800-5 recommended)
- Inorganic Ventures (Christiansburg, VA) chlorate standard (part number [P/N] ICCLO31)
- Inorganic Ventures perchlorate standard (P/N ICCLO41)
- Dionex combined seven anion standard II (Thermo Scientific Dionex P/N 056933) containing the following chemicals with their respective Chemical Abstracts Service (CAS) numbers:
 - 20 mg/L (nominal) fluoride CAS 7681-49-4
 - 30 mg/L (nominal) chloride CAS 7647-14-5
 - 100 mg/L (nominal) nitrite CAS 7632-00-0
 - 100 mg/L (nominal) bromide CAS 7647-15-6
 - 100 mg/L (nominal) nitrate CAS 7631-99-4
 - 100 mg/L (nominal) sulfate CAS 7757-82-6
 - 200 mg/L (nominal) phosphate CAS 7778-77-0
- Dionex combined six cation standard (Thermo Scientific Dionex P/N 046070) containing the following chemicals with their respective CAS numbers:
 - 50 mg/L (nominal) lithium CAS 7439-93-2
 - 200 mg/L (nominal) sodium CAS 7440-23-5
 - 250 mg/L (nominal) ammonium CAS 14798-03-9
 - 500 mg/L (nominal) potassium CAS 7440-09-7
 - 250 mg/L (nominal) magnesium CAS 7439-95-4
 - 500 mg/L (nominal) calcium CAS 7440-70-2

The following common laboratory equipment and supplies were used:

- 15–20 mL I-Chem vials (Thomas Scientific; Swedesboro, NJ) and/or plastic equivalents,
- autosampler vials and caps,
- pipetters and disposable tips covering the range of 10 μ L to 10 mL,
- waste container, and
- laboratory cleaning wipes.

Specialized equipment and supplies that were used for this procedure were as follows:

- Thermo Scientific Dionex ICS-2100 integrated RFIC system AS-AP autosampler (P/N 074926);
- Thermo Scientific Dionex ASRS 500 2 mm suppressor (P/N 082541);
- Thermo Scientific Dionex IonPac AG20 2 \times 50 mm guard column (P/N 063066);
- Thermo Scientific Dionex IonPac AS20 2 \times 250 mm analytical column (P/N 063065);
- Thermo Scientific Dionex RFIC eluent generator cartridge, EGC III KOH (P/N 074532);
- Thermo Scientific Dionex CERS 500 4 mm suppressor (P/N 082543);
- Thermo Scientific Dionex IonPac CG18 2 \times 50 mm guard column (P/N 062880);
- Thermo Scientific Dionex IonPac CS18 2 \times 250 mm analytical column (P/N 062878); and
- Thermo Scientific Dionex RFIC eluent generator cartridge, EGC III MSA (P/N 074535).

3.2 Methods

To perform the methods used in this study, all anion stock solutions and the dilutions from those stock solutions must be remade after the manufacturer's expiration date, all cation stock solutions and the dilutions from those stock solutions were remade after the manufacturer's expiration date, and all stock solutions were stored at or below 8 $^{\circ}$ C in a refrigerator.

3.2.1 Preparation of Stock Standard Solutions

The standard solutions were made in 15 mL plastic I-Chem vials. Dilutions of the standard solutions were prepared by pipetting the solvent of NERL water into a tube and then pipetting in the standard solution. Preparation of the seven anion, chlorate, and perchlorate calibration standard solutions (Tables 1 through 3) were made by adding 10 mL of NERL water to six clean plastic bottles (at least 15 mL in size). A primary standard was made from the Dionex combined seven anion standard II solution by adding 10 mL to a single plastic bottle that was capable of holding 20 mL total.

Table 1. Nominal Concentrations of Anion Calibration Standards from Stocks

Property	F ⁻	Br ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Cl ⁻	Amount of Standard Solution (mL)	Amount of Water (mL)	Final Total Volume (mL)
Nominal concentration of anion in the standard stock solutions (mg/L)	20.2	101	99.8	99.0	152	151	29.9	10	10	20.0
Final nominal concentration of anion (µg/mL)	10.1	50.5	49.6	49.5	76	75.5	14.9			

Then the perchlorate and chlorate standards were added to the primary standard. This was done by adding 2 mL of each the perchlorate and chlorate standard to the primary standard solution made as described in the first paragraph of Section 3.2.1.

Table 2. Nominal Concentrations of Chlorate and Perchlorate Calibration Standards from Stocks

Property	ClO ₃ ⁻	ClO ₄ ⁻	Stock Added (mL)	Water (mL)	Final Volume (mL)
Nominal Concentration of Anion in the Stock Solutions (mg/L)	1002	1004	2	18	20.0
Final Nominal Concentration of Anion (µg/mL)	100.2	100.4			

From the primary standard, the dilutions listed in Tables 3 and 4 were made in separate, clean plastic bottles for the standard curve.

Table 3. Nominal Concentrations of Anion Calibration Standards from Primary Standard

Containers	Volume of Primary Standard (µL)	Final Volume (mL)	Primary Standard (µg/mL)								
			F ⁻	Br ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Cl ⁻	ClO ₃ ⁻	ClO ₄ ⁻
			10.1	50.5	49.6	49.5	76.0	75.5	14.9	100.2	100.4
Bottle 1	200	5	0.40	2.02	1.98	1.98	3.04	3.02	0.60	4.01	4.02
Bottle 2	500	5	1.01	5.05	4.96	4.95	7.60	7.55	1.49	10.02	10.04
Bottle 3	1000	5	2.02	10.10	9.92	9.90	15.20	15.10	2.98	20.04	20.08
Bottle 4	1500	5	3.03	15.15	14.88	14.85	22.80	22.65	4.47	30.06	30.12
Bottle 5	2500	5	5.05	25.25	24.80	24.75	38.00	37.75	7.45	50.10	50.20
Bottle 6	3500	5	7.07	35.35	34.72	34.65	53.20	52.85	10.43	70.14	70.28

Table 4. Nominal Concentrations of Cation Calibration Standards

Amount of NERL Water (µL)	Amount of Cation Standard Solution (µL)	Final Volume (mL)	Final Concentration (mg/L)					
			Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
9950	50	10	0.247	0.995	1.24	2.475	1.23	2.495
9925	75	10	0.3705	1.4925	1.86	3.7125	1.845	3.7425
9900	100	10	0.494	1.99	2.48	4.95	2.46	4.99
9800	200	10	0.988	3.98	4.96	9.9	4.92	9.98
9600	400	10	1.976	7.96	9.92	19.8	9.84	19.96
9500	500	10	2.47	9.95	12.4	24.75	12.3	24.95

3.2.2 Quality Assurance Samples

For the method blank, a sample of NERL water (from the same lot) was processed through the entire sample preparation procedure with each batch of samples. The method blank was then analyzed with the samples.

For the reagent blank, a sample of NERL water was run before and after the continuing calibration verification sample to ensure that no carryover occurred.

3.2.3 Sample Analysis

To prepare the Thermo Fisher ICS-2100 instrument for analysis, necessary performance verification was completed in accordance with internal operating procedures.³ The

calibration curve samples and precision and accuracy samples were loaded into the autosampler, and the sequence was run.

4. RESULTS AND DISCUSSION

4.1 Calibration Curves

Calculations of the analyte concentration present in the sample were based on the linear or quadratic regression line fitted to the original calibration. All samples with concentrations of target analytes that exceeded the calibration range were diluted to a concentration within the calibration range. If a sample was diluted, the concentration determined by the calibration curve was multiplied by the dilution factor.

The concentrations used in this study were optimized to produce linear regression fits for the calibration curves. The resultant calibration curve must either be linear and have a coefficient of determination (r^2) greater than or equal to 0.990 or be quadratic and have an r^2 greater than or equal to 0.995. The concentration of an unknown sample was determined from the standard curve constructed from analyses of the standards.

4.2 Relative Percent Differences

The precision of the sample analysis was determined by calculating the relative percent difference between the measured and expected concentrations:

$$\left(\frac{C_M - C_E}{\text{Average } (C_M + C_E)} \right) \times 100\% \quad (1)$$

where C_M is the concentration measured by the instrument, and C_E is the expected concentration.

Each ion had a minimum of five valid points in the calibration curve (Tables 3 and 4).

4.3 Method Detection Limits (MDLs)

An MDL was performed as described in Chapter 1 of the EPA publication SW-846.⁴ Five replicate solutions with all analytes were prepared by spiking the matrix with the analyte at a concentration equal to three to five times the estimated MDL. The solutions were analyzed in random order. The MDL was determined by multiplying the appropriate one-sided 99% t statistic (3.50 for seven measurements, as done for anions; 2.57 for six measurements, as done for cations) by the standard deviation (SD) of the replicate measurements:

$$\text{MDL} = \text{SD of } n \text{ replicates} \times t \quad (2)$$

The MDLs for the anions and cations are listed in Tables 5 and 6, respectively.

Table 5. MDL Values for the Anions

MDL (mg/L)	F ⁻ 0.202 mg/L	Cl ⁻ 0.298 mg/L	NO ₂ ⁻ 0.99 mg/L	Br ⁻ 1.01 mg/L	NO ₃ ⁻ 0.995 mg/L	SO ₄ ²⁻ 1.49 mg/L	PO ₄ ³⁻ 1.50 mg/L	ClO ₃ ⁻ 1.005 mg/L	ClO ₄ ⁻ 1.00 mg/L
	0.0520	0.0613	0.0613	0.1882	0.1925	0.3719	0.3423	0.2042	0.2110

Table 6. MDL Values for the Cations

MDL (mg/L)	Li ⁺ 0.247 mg/L	Na ⁺ 0.995 mg/L	NH ₄ ⁺ 1.24 mg/L	K ⁺ 2.475 mg/L	Mg ²⁺ 1.23 mg/L	Ca ²⁺ 2.495 mg/L
	0.0089	0.058	0.081	0.23	0.048	0.302

4.3.1 Precision and Accuracy Study

For the precision and accuracy study, three solutions at each calibration level were prepared and analyzed in random order. This procedure was repeated on a second day to prepare a separate batch of standards at each concentration level for a total of six analyses at each calibration level. Concentrations of the tested calibration levels are listed in Tables 7 and 8.

Table 7. Nominal Concentrations of the Anion Precision and Accuracy Levels

Calibration Level	Concentration (mg/L)								
	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	ClO ₃ ⁻	ClO ₄ ⁻
1	0.404	0.596	1.99	2.02	1.99	2.98	3	2.01	2
2	1.01	1.49	4.97	5.05	4.97	7.45	7.5	5.02	5.01
3	2.02	2.98	9.94	10.1	9.94	14.9	15	10	10
4	3.03	4.47	14.9	15.2	14.9	22.4	22.5	15.1	15.1
5	5.03	7.45	24.9	25.3	24.9	37.3	37.5	25.1	25.1
6	7.07	10.4	34.8	35.4	34.8	52.2	52.5	35.1	35.1
7	10.1	14.9	49.7	50.5	49.7	74.5	75	50.2	50.1

Table 8. Nominal Concentrations of the Cation Precision and Accuracy Levels

Level	Concentration (mg/L)					
	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
1	0.247	0.995	1.24	2.475	1.23	2.495
2	0.3705	1.4925	1.86	3.7125	1.845	3.7425
3	0.494	1.99	2.48	4.95	2.46	4.99
4	0.988	3.98	4.96	9.9	4.92	9.98
5	1.976	7.96	9.92	19.8	9.84	19.96
6	2.417	9.95	12.4	24.75	12.3	24.95

The relative standard deviations (RSDs) of the three solutions at each calibration level were calculated using the following equation:

$$RSD = \left(\frac{SD \text{ of replicates}}{\text{average result}} \right) \quad (3)$$

4.3.2 Measurement of Uncertainty

The measurement uncertainty for the three solutions at each calibration level was determined in accordance with EC/B FAC procedures (based on the SD of a minimum of six replicates of each calibration level, analyzed over 2 days). The major sources contributing to the measurement of uncertainty were errors from the calibration curves and process repeatability. These sources were measured during the method validation and then combined to determine the overall uncertainty at 95% confidence (Tables 9 and 10).

Table 9. Measurement Uncertainty for Anions

Analyte	Concentration (mg/L)	Measurement Uncertainty (Anions) (%)
F ⁻	*0.404	499
	1.01	187
	2.02	88
	3.03	58
	5.03	64
	7.07	48
	10.1	45

(table continued)

Table 9. Measurement Uncertainty for Anions (continued)

Analyte	Concentration (mg/L)	Measurement Uncertainty (Anions) (%)
Cl ⁻	*0.596	472
	1.49	180
	2.98	85
	4.47	59
	7.45	90
	10.4	66
	14.9	66
NO ₂ ⁻	*1.99	307
	4.97	118
	9.94	56
	14.9	39
	24.9	52
	34.8	40
	49.7	37
Br ⁻	*2.02	405
	5.05	153
	10.1	72
	15.2	48
	25.3	59
	35.4	45
	50.5	45
NO ₃ ⁻	*1.99	482
	4.97	180
	9.94	85
	14.9	56
	24.9	65
	34.8	48
	49.7	47
SO ₄ ²⁻	*2.98	685
	7.45	254
	14.9	120
	22.4	78
	37.3	79
	52.2	60
	74.5	57

(table continued)

Table 9. Measurement Uncertainty for Anions (continued)

Analyte	Concentration (mg/L)	Measurement Uncertainty (Anions) (%)
PO ₄ ³⁻	*3	769
	7.5	283
	15	134
	22.5	87
	37.5	82
	52.5	63
	75	61
ClO ₃ ⁻	*2.01	510
	5.02	190
	10	90
	15.1	59
	25.1	65
	35.1	50
	50.2	48
ClO ₄ ⁻	*2	365
	5.01	152
	10	78
	15.1	54
	25.1	65
	35.1	50
	50.1	49

* Denotes practical quantitation limits identified through precision and analysis and measurement of uncertainty.

Table 10. Measurement Uncertainty for Cations

Analyte	Concentration (mg/L)	Measurement Uncertainty (Cations) (%)
Li ⁺	*0.247	62
	0.3705	51
	0.495	31
	0.988	57
	1.976	30
	2.47	11
Na ⁺	*0.995	67
	1.4925	55
	1.99	33
	3.98	56
	7.96	32
	9.95	104
NH ₄ ⁺	*1.24	94
	1.86	74
	2.48	50
	4.96	32
	9.92	26
	12.4	26
K ⁺	*2.475	56
	3.7125	48
	4.95	30
	9.9	17
	19.8	12
	24.75	12
Mg ²⁺	*1.23	58
	1.845	48
	2.46	30
	4.92	18
	9.84	12
	12.3	11
Ca ²⁺	*2.495	62
	3.7425	42
	4.99	31
	9.98	20
	19.96	12
	24.95	12

* Denotes practical quantitation limits identified through precision and analysis and measurement of uncertainty.

5. CONCLUSIONS

IC is a viable method for quantitative analysis of nine anions and six cations, which include the popular compound, ammonium nitrate. Calibration curves were valid for a minimum of six points for all of the anions and cations. MDLs were calculated for each analyte. The MDLs for ammonium and nitrate were 1.24 and 1.99 mg/L, respectively. Measurements of uncertainty were also calculated for ammonium and nitrate at each calibration level. In addition, measurements of uncertainty were calculated for each anion and cation in the sample cocktails. Whether a sample is screened for ammonium nitrate or potassium chloride, the IC system can produce quantitative results for a variety of anions and cations in NERL-grade water.

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ACRONYMS AND ABBREVIATIONS

CAS	Chemical Abstracts Service
CCDC CBC	U.S. Army Combat Capabilities Development Command Chemical Biological Center
EC/B FAC	U.S. Army Edgewood Chemical Biological Center Forensic Analytical Center
IC	ion chromatography
IEC	International Electrotechnical Commission
IED	improvised explosive device
ISO	International Organization for Standardization
MDL	method detection limit
P/N	part number
r^2	coefficient of determination
RFIC	reagent-free ion chromatography
RSD	relative standard deviation
SD	standard deviation

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