

# Analysis of commercial explosives by single-column ion chromatography

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## ABSTRACT

Commercial explosives utilize inorganic salts as an inexpensive and effective oxidizing agent. Important performance criteria of commercial explosives are gathered from the analysis of these salts in the formulation. An optimum ratio of inorganic salts to fuel oil needs to be maintained to produce complete combustion and maximum energy. This information is quickly and accurately provided by an ion chromatographic method described here. The anion analysis is performed on an hydroxyethylmethacrylate-based macroporous copolymer-based anion-exchange column, which provides good peak shapes for nitrate. Analyzing both monovalent and divalent cations in a single chromatographic step is made possible by new cation-exchangers. The dual-column method for the simultaneous determination of anions and cations was applied to the analysis of nitrate, ammonium, hexamethylenetetramine, calcium and magnesium in a single chromatographic analysis of less than 35 min. A comparison between the traditional, wet chemistry methods commonly used for commercial explosive analysis and this new ion chromatographic method is presented.

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## INTRODUCTION

Commercial explosives used in mining and construction utilize ammonium nitrate as an inexpensive and effective oxidizing agent. Fertilizer grade ammonium nitrate is mixed with fuel oil to formulate a safe non nitroglycerin alternative to dynamite. This ammonium nitrate-fuel oil mixture (ANFO) is easy to manufacture at a low cost. ANFO is very hygroscopic and is used only in large-diameter boreholes because it will not sustain a detonation in small-diameter holes. These limitations of ANFO led to the development of explosives with better water resistance and excellent performance. These aqueous-based ammonium nitrate explosives include slurries and water-in-oil emulsions. Greater water resistance and sensitivity of slurries and emulsions is provided by the intimacy between fuel and oxidizer. Due to their low cost, excellent performance and superior safety characteristics, ANFO and other ammonium nitrate explosives now account for 96.6% of the total commercial explosives market [1].

The optimum ratio of ammonium nitrate to fuel

oil in ANFO, 94.5:5.5, is necessary to stoichiometrically balance the combustion process. With this ratio there will be sufficient oxygen in the formulation to react with all the fuel. Complete combustion is achieved at this level to produce the highest energy. The theoretical reaction is shown in eqn. 1 [2].



In the formulation of aqueous-based slurries and emulsions a large amount of ammonium nitrate must be used to react with a small amount of fuel to maintain this necessary oxygen balance. This ratio of ammonium nitrate to fuel in emulsion is approximately 90:10. Dry ammonium nitrate is added to the emulsion to provide the additional oxygen necessary to balance the combustion process. Ingredients of commercial explosive are selected to vary the energy, detonation sensitivity, oxygen balance, rheology and stability. Other oxidizer salts that are used include sodium nitrate, calcium nitrate, sodium perchlorate and amine nitrates. By varying the ingredients it is possible to customize commercial to meet specific requirements.

It is this customization that necessitates the anal-

ysis of the inorganic salts in the formulated product. Formulations that do not perform as expected are analyzed to confirm that the desired oxygen balance is met. In addition to troubleshooting, analysis of the oxidizer salts is necessary for process control and quality assurance. The traditional wet chemical methods, which are both tedious and time consuming, are being replaced by chromatographic methods. In the past, these chromatographic methods included the analysis of the anions and cations of the inorganic salts on separate columns. Monovalent cations have been separated on cation-exchange columns with a dilute mineral acid eluent. Divalent cation analysis was achieved with the same column by changing to a divalent eluent. For example, a single-column ion chromatography (IC) method was used to determine cations in commercial explosives. A Wescan Cation/R poly(styrene-divinylbenzene) (PS-DVB) column, was used in conjunction with 3.9 mM nitric acid to provide the separation of sodium, ammonium, and monomethylamine. The same column was used with ethylenediamine for the determination of calcium [3]. Chemically suppressed IC methods have also been used for the determination of anions and cations in water-based explosives and residues. A UV detector was used in line with the conductivity detector to provide detection of perchlorate and nitrate on an anion exchange column using a  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  eluent. Monovalent and divalent cations were separated on a cation-exchange column with hydrochloric acid and hydrochloric acid-phenylenediamine eluents, respectively [4].

A new single-column IC method for the analysis of ammonium nitrate in a commercial emulsion and slurry explosives using new anion and cation column technology and a dual-column technique will be compared to the traditional wet chemical analysis. The nitrate analysis is performed on an anion-exchange column packed with a hydroxyethyl methacrylate-based macroporous copolymer. This column provides improved peak shapes for polarizable anion, such as nitrate, when compared with PS-DVB based anion columns [5]. The ability to separate monovalent and divalent cations present in commercial explosives in one isocratic run is provided by a commercial version of a silica-based polymer coated stationary phase developed by Schomburg *et al.* [6]. A dual-column technique for

the simultaneous analysis of anions and cations is used to obtain the total inorganic composition of the formulation in one chromatographic run of approximately 35 min duration.

## EXPERIMENTAL

### *Chromatography*

All chromatographic equipment, columns and reagents, unless stated otherwise, were obtained from Alltech Assoc. (Deerfield, IL, USA). Chromatography was performed on a system which consists of a Model 325 metal-free high-performance liquid chromatography (HPLC) pump, a 9125 injection valve (Rheodyne, Reno, NV, USA) with a 100- $\mu\text{l}$  sample loop, a column oven (Timerline, Boulder, CO, USA) and an Alltech Model 320 conductivity detector. A Rheodyne Model 9000 switching valve mounted to a Universal Valve Actuator was used to direct the flow through or around the cation-exchange column. An SP 4400 Chromjet integrator (Spectra-Physics, Santa Clara, CA, USA) was used to record the separation and control the switching valve. The Universal Anion Column (50 mm  $\times$  4.6 mm I.D.) packed with hydroxyethyl methacrylate copolymer anion exchanger and a Universal Cation Column (100 mm  $\times$  4.6 mm I.D.) packed with a silica coated with polybutadiene-maleic acid copolymer were used to provide the separation.

### *Distillation apparatus*

An all-glass still was used for the distillation of the ammonia in the traditional wet chemistry methods. It consisted of a 2-l flask, connected to a spray trap, water-cooled condenser, and a long delivery tube which extends to the bottom of a 250-ml Erlenmeyer flask.

### *Reagents*

All reagents used for the traditional wet and chromatographic methods were prepared using NBS- or ACS-grade materials. The eluent used for the chromatographic separation was phthalic acid. A stock solution was prepared by dissolving the ACS-grade reagent in methanol. This solution was diluted to make 5 mM phthalic acid. The pH of this solution, approximately 2.9, was not adjusted. All standards, eluents and dilutions were prepared with deionized HPLC-grade water.

### Samples and sample preparation

Samples of commercial explosives were obtained from commercial suppliers along with the quantitative results of the determination of ammonia by the traditional wet chemical method. Prior to chromatographic or wet chemistry analysis, 10 g of the commercial explosives were homogenizing and dissolved in 100 ml of HPLC-grade methanol. These solutions were diluted and filtered before chromatographic determination. No other sample preparation was necessary. The traditional wet chemical method utilized aliquots of the explosive-methanol solution.

### Procedures

**Traditional wet chemical methods.** The ammonium nitrate concentration is determined by a distillation procedure for ammonia nitrogen in water based on the EPA Method 350.2 [7]. This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen. An aliquot of the digested explosive sample is weighed into a Kjeldahl flask. A 50-ml volume of a 50% ammonium hydroxide solution is added to adjust the pH of the sample. The flask is filled with 220 ml of water and distilled into 2% boric acid. The ammonia in the distillate is titrated with 0.05 M sulfuric acid to the endpoint determined by bromocresol green indicator. The volume of titrant is corrected by titrating a blank to the same endpoint.

**Chromatographic method.** The Universal Anion Column was used with an eluent of 5 mM phthalic acid to determine the nitrate concentration in the commercial explosives. The Universal Cation Column was used with the same eluent to provide the separation of monovalent and divalent cations. A dual-column technique for the simultaneous analysis of anion and cations, described previously [8,9], was used to provide a complete ionic quantification of the commercial explosive formulation in one chromatographic run. With the eluent passing through both columns, the sample is injected. The anions in the sample are retained on the anion-exchange column but the cations will pass through the column unretained. Once the cations reach the head of the cation column, the switching valve is actuated and the eluent bypasses the cation column. This allows the anions to be separated on the anion column and passed on to the detector. After the anion

analysis is complete the switching valve diverts eluent through the cation column, to separate and elute the cations left at the inlet of the column.

### RESULTS AND DISCUSSION

Standard wet chemical methods are often used for the quantification of the inorganic salts in commercial explosives. Although these standard methods have been well studied and can be accurate and reproducible, the analysis is time consuming taking approximately up to 5 h per sample depending on the composition. The ammonium nitrate concentration is determined by the EPA method of distillation and titration. This method determines the concentration of ammonia in the sample. In calculating the ammonium nitrate present in the sample, it is assumed that all of the ammonia is present in the form of ammonium nitrate.

IC provides a method of the analysis of inorganic oxidizer salts in commercial explosives that can be rapid and sensitive. The ammonia concentration can be determined by IC in only 6 min. The anion analysis of nitrate in a commercial emulsion explosive on the Universal Anion Column using 5 mM phthalic acid eluent is shown in Fig. 1. The analysis of ammonia in the emulsion explosive separated on

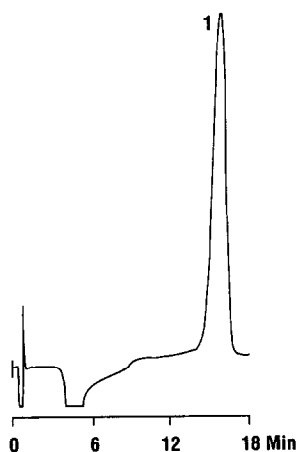


Fig. 1. Nitrate analysis of commercial emulsion explosive. Chromatographic conditions: column, 100 mm  $\times$  4.6 mm I.D.; packing, Universal Cation; eluent, 5 mM phthalic acid, pH unadjusted; flow-rate, 1 ml/min; detector, conductivity; range, 1  $\mu$ S cm full scale. Peak 1 = nitrate.

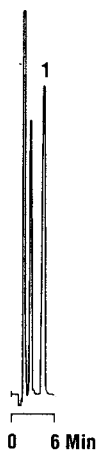


Fig. 2. Ammonia analysis of commercial emulsion explosive. Chromatographic conditions as in Fig. 1. Peak 1 = ammonium.

the Universal Cation Column using the same eluent is shown as Fig. 2. The cation analysis can also determine any secondary salts, such as sodium, organic amines, calcium and magnesium in the formulation. Fig. 3 displays the separation of ammonia, hexamethylenetetramine, magnesium and calcium in reagent water.

Although the use of IC with the new anion- and cation-exchange column allows a rapid and complete analysis of the ions present in the formulation, performing the anion and cation analysis indepen-

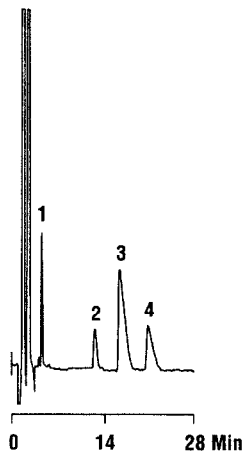


Fig. 3. Cation analysis of oxidizer salts. Chromatographic conditions as in Fig. 1. Peaks: 1 = ammonium; 2 = hexamethylenetetramine; 3 = magnesium; 4 = calcium.

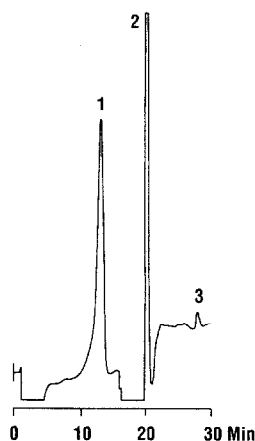


Fig. 4. Simultaneous analysis of anions and cations in commercial slurry explosive. Chromatographic conditions: anion column, 50 mm  $\times$  4.6 mm I.D.; anion packing, Universal Anion; cation column, 100 mm  $\times$  4.6 mm I.D.; cation packing, Universal Cation; eluent, 5 mM phthalic acid, pH unadjusted; flow-rate, 1 ml/min; detector, conductivity; range, 1  $\mu$ S cm full scale. Peaks: 1 = nitrate; 2 = ammonium; 3 = hexamethylenetetramine.

dently can be time consuming. A dual-column technique for the simultaneous analysis of anion and cations provides the analysis of ammonium and nitrate in 20 min. A complete ionic quantification of the commercial explosive formulation, including anions and monovalent and divalent cations, can be obtained in one chromatographic run of less than 35 min. The simultaneous analysis of ammonium, hexamethylenetetramine and nitrate using this dual-column technique for the analysis of a commercial slurry explosive is shown in Fig. 4.

The results of the traditional wet method for the analysis of ammonium in the emulsion explosive are shown in Table I. The chromatographic results of the analysis of a commercial emulsion explosive containing ammonium nitrate as an oxidizer salt is shown in Table II. The ammonium nitrate concentration of a commercial slurry explosive was also analyzed. The results of the analysis can be found in Table III. These chromatographic results were obtained by comparing each peak area to a three-point external standard calibration curve. Instead of assuming that all the ammonia present is present as the ammonium nitrate salt, IC can determine both the anion and cations. Using this method the exact concentration of the ammonium nitrate in the

TABLE I

## TRADITIONAL WET METHOD RESULTS: AMMONIUM NITRATE ANALYSIS IN COMMERCIAL EMULSION EXPLOSIVE

Analyte	Relative S.D. (%) (n = 2)	% of ion in sample	% of NH <sub>4</sub> NO <sub>3</sub> in sample
Ammonia	1.45	14.16	62.97

formulation can be confirmed. As shown in Table II, there is excellent correlation between the single-column and dual-column method results for the analysis of ammonium and nitrate. These results indicate that as much as 0.6% or 4 mM of the ammonium was present in the formulation may be in a form other than ammonium nitrate. Without the ability to analyze the nitrate concentration this apparent discrepancy would not have been identified. The value for ammonium found by traditional wet

chemical methods and both single-column and dual-column chromatographic methods correlate well within the experimental precision of both methods.

A 6-min cation-exchange separation of ammonium can replace the traditional wet chemical method that can take as much as 40 min. The complete analysis of ammonium and nitrate can be achieved in 20 min using the dual-column technique. The sample throughput of this dual-column IC method can be

TABLE II

## CHROMATOGRAPHIC RESULTS OF AMMONIUM NITRATE ANALYSIS IN COMMERCIAL EMULSION EXPLOSIVE

Dilution 110.6 mg sample/l.

Analyte	Method	Concentration		Relative S.D. (%) (n = 3)	% of ion in sample	% of NH <sub>4</sub> NO <sub>3</sub> in sample
		ppm	mM			
Ammonium	Cations only	16.33	0.91	0.22	14.76	65.51
	Dual column	16.52	0.92	0.25	14.93	66.38
Nitrate	Anions only	55.09	0.88	1.18	49.81	64.28
	Dual column	545.54	0.88	1.69	49.31	63.62

TABLE III

## CHROMATOGRAPHIC RESULTS OF AMMONIUM NITRATE ANALYSIS IN COMMERCIAL SLURRY EXPLOSIVE

Dilution 161.3 mg sample/l.

Analyte	Method	Concentration		Relative S.D. (%) (n = 3)	% of ion in sample	% of NH <sub>4</sub> NO <sub>3</sub> in sample
		ppm	M			
Ammonium	Dual column	2348	0.130	0.05	14.55	64.70
	Cations only	2338	0.130	0.84	14.49	64.32
Nitrate	Anions only	8335	0.134	1.75	51.68	66.67
	Dual column	8242	0.133	1.09	51.10	65.93

as much as 20 commercial explosive samples per 8-h day. Automation of the IC system with the addition of a autosampler and an automated switching valve can allow unattended operation for continuous analysis.

If calcium, magnesium or organic amines are present in the commercial explosives IC can replace hours of individual traditional wet chemical methods. The analysis of these components in the sample can be obtained in 35 min with the dual-column technique. The traditional wet chemistry method for calcium and magnesium is ASTM Method D 511-88 [10]. This complexometric titration with EDTA requires that two solutions of the sample be analyzed, one at pH of 10 for the determination of calcium plus magnesium and one at pH of 12 for the determination of calcium alone. Magnesium is then determined by the difference between these two measurements. Some amines will interfere with the traditional wet chemistry method for the determination of ammonia. These include amines in the formulation that will breakdown to ammonia during the distillation process, such as methylammonium salts of hexamethylenetetramine. IC provides the ability to determine ammonium and amines simultaneously.

In addition to the increased sample throughput with IC, the variety and consumption of reagents is reduced compared to traditional wet chemistry methods. The consumption of reagents for the dual-column method is less than 40 ml of 5 mM phthalic acid per sample. The reagents necessary for the digestion and distillation of one sample can be as much as 50 ml of 50% sodium hydroxide, 50 ml of 2% boric acid, 25 ml of 0.1 M HCl. The IC method eliminates the formulation of these reagents and the time consuming process of standardizing the titrant.

## CONCLUSION

The necessity of analyzing the inorganic oxidizer salts in commercial explosives is made less consum-

ing by IC methods. The anion analysis is performed on an hydroxyethyl methacrylate-based macroporous copolymer anion-exchange column to provide good peak shapes for nitrate. The analysis of both mono and divalent cations in the formulations can be achieved with the new cation-exchange column. The dual-column technique provides the simultaneous determination of the mono and divalent cation along with all anions in the commercial explosive. This technique allows for the analysis of ammonium nitrate in 20 min and a complete analysis of the formulation within 35 min. There is good correlation between the traditional wet chemistry and dual-column IC method results for the analysis of ammonium nitrate. Time and money are saved by the rapid analysis time, multicomponent analysis, lower reagent consumption and elimination of titrant standardization.

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