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Ion chromatography of energetic materials at Sandia National Laboratories

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Abstract

This paper is a survey of ion chromatography (IC) methods used at Sandia National Laboratories to characterize energetic materials. Information is given for the analysis of a variety of materials including pyrotechnic, explosive, and propellant materials that contain perchlorate, smoke compositions, a primer mixture, and explosive materials such as pentaerythritoltetranitrate (PETN). An appendix contains details for those who may wish to apply the analyses in their laboratories. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ion chromatography; Pyrotechnic; Energetic materials; Explosives; Propellants

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1. Introduction

Sandia National Laboratories[1] is operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy (DOE). The Explosive Subsystems and Materials Department is located in the Explosives Component Facility in Albuquerque, New Mexico, as shown in Fig. 1. This department is active in the characterization of energetic materials (explosives, propellants, and pyrotechnics). Ion chromatography (IC) is one of the tools used to assess degradation reactions in energetic materials for surveillance and aging/compatibility studies. IC is also used to assess purity in the development, qualification, and processing of energetic materials. Additionally, IC can be used for the identification of unknowns.

This paper is a survey describing IC methods used at the Explosives Component Facility and contains information for the analysis of a variety of energetic materials—both inorganic and organic. Details of the analyses are given in Appendix A for those who may want to apply them in their laboratories. The instrumentation that is used for the IC analysis of energetic materials at Sandia National Laboratories is manufactured by Dionex Corporation, and references to specific column sets are to those manufactured by Dionex as well.

Ammonium, chloride, chlorate, and nitrate are a few of the common ions of interest to those who analyze energetic materials. IC can be used to separate, identify, and quantitate these charged species [1]. An IC system is composed of eluent, pump, injection valve, column, suppressor, and detector as shown in Fig. 2. Eluents are dilute aqueous solutions of bases, acids, or salts of weak acids and are pumped through columns whose packing contains either negative groups such as sulfonate or carboxylate for the analysis of cations or positive groups such as quaternary amines for the analysis of anions. Separation occurs when ions have different affinities for the column packing. The suppressor

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[1] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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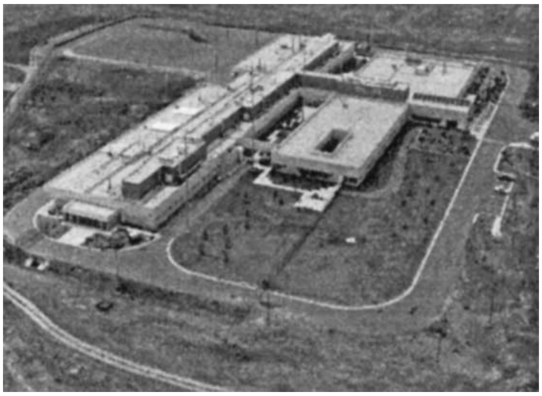

Fig. 1. Aerial view of the explosives component facility, Sandia National Laboratories, Albuquerque, New Mexico.

chemically renders the eluent less conductive and therefore increases the sensitivity of the analytes to the detector. Conductivity detectors are usually used although electrochemical and ultraviolet-visible detectors can be used for special applications.

Ion concentrations are measured in a solution that is representative of the sample and are related to the concentration in energetic materials as shown in Eq. (1):

$$C\,(\mu g/g) = \frac{A\,(\mu g/ml) \times B\,(ml)}{\text{Sample weight (g)}} \quad (1)$$

where A is the concentration of the ionic species in solution as determined by analysis, B the number of milliliters used to prepare the sample, and C is the concentration of the ionic species in the energetic material sample.

2. Prominence of perchlorate-containing energetic materials at Sandia National Laboratories

During the 1970s, a policy decision was made at Sandia National Laboratories to stop using primary explosives in various energetic material designs due to concern about the safety of handling powders and accidental initiation of devices by electrostatic discharge (ESD). The primary explosives, lead azide and lead styphnate, were typically used and were replaced by cobalt(III) coordination compounds or by pyrotechnic formulations based on titanium/titanium subhydride and potassium perchlorate. The replacement materials do not contain lead, which also makes them environmentally more favorable materials.

Explosives based on cobalt coordination compounds were developed with Unidynamics, Inc. (now Pacific Scientific) and were found to undergo a deflagration-to-detonation transition when confined, which makes them suitable for hot wire initiated detonators when a detonation output is necessary [2]. Friction, impact, and ESD data show a material approximately an order of magnitude less sensitive to initiation than lead azide. One particular cobalt coordination compound, 2-(5-cyano-tetrazolato)pentaamminecobalt(III) perchlorate (CP), has been used in DOE detonator designs since the late 1970s. The chemical structure of CP is shown in Fig. 3.

Blends of potassium perchlorate with either titanium or titanium subhydride are now used in place of primary explosives in devices such as igniters and actuators when a gaseous, hot particulate, or work output is necessary [3]. Titanium/potassium perchlorate mixtures are used in applications where ESD sensitivity is not an issue. In applications where ESD is an issue, special titanium subhydride powders are used with potassium perchlorate. Studies have shown that $TiH_x/KClO_4$ is ESD insensitive for $x > 0.6$; however, for $x = 2$, $TiH_2/KClO_4$ mixtures are not as thermally stable and are more susceptible to low temperature ignition failures than material with a lower hydrogen content. Therefore, the $TiH_x/KClO_4$ of choice today for Sandia designed applications, such as actuators, is $TiH_{1.65}/KClO_4$.

3. Anion analysis of perchlorate-containing energetic materials

The decomposition reaction of $TiH_x/KClO_4$ ($x =$ 0–2) produces chloride ion as shown in Fig. 4. A study

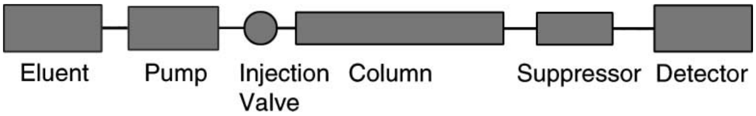

Fig. 2. Ion chromatography system.

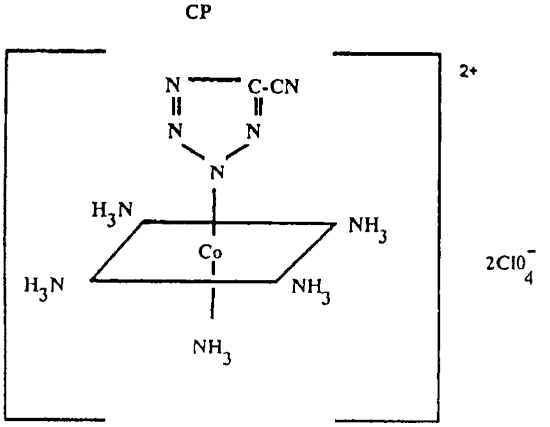

Fig. 3. Structure of 2-(5-cyano-tetrazolato)pentaamminecobalt(III) perchlorate.

of the thermal decomposition of CP has shown that chloride is a decomposition product of CP as well [4]. Thus, the analysis of chloride concentration in these kinds of materials is needed to monitor decomposition and reactions due to incompatibility and aging. In some cases, additional anions are of interest. Methods for anion analysis of these materials have also been found to be applicable to the many other perchlorate containing energetic materials such as heat powders ($Fe/KClO_4$) and composite propellant formulations, which contain ammonium perchlorate.

The perchlorate matrix provides a challenge for chloride analyses because perchlorate moves slowly through columns under conditions needed for standard anion analysis and is present in great excess. On a standard anion column set such as the Ion Pac AG4/AS4, perchlorate shortens the retention time of chloride, which pushes it into the region of the chromatogram with no conductivity, i.e. the "water dip" which arises from the sample water matrix. Good quantitation can not be accomplished if a peak is partially in the "water dip", and it takes a minimum of 60 min to elute the perchlorate. Likewise the newer Ion Pac AG11/AS11 is not acceptable for this analysis. In the presence of perchlorate, the chloride peak shape is poor, and the baseline in the chloride elution region of the chromatogram is also poor resulting in inaccurate quantitation, especially at low levels of chloride of just a few tenths of a μg/ml. The older Ion Pac AG5A-5 μm/AS5A-5 μm has been found to be an excellent column set for analysis of chloride in the presence of excess perchlorate. The peak shape and baseline are excellent, as shown in Fig. 5 for a 1 μg/ml concentration of chloride in a matrix of about 5000 μg/ml perchlorate. The eluent is 15 mM sodium hydroxide, and once the chloride has eluted, the concentration can be stepped to 200 mM to elute perchlorate in 35 min. More recent activities in Dionex suppressor development limit the concentration of sodium hydroxide that can flow through the suppressor to 100 mM, however, and so provision has to be made to bypass the suppressor for the portion of the analysis that uses 200 mM sodium hydroxide.[2] This column set does not resolve nitrate and chlorate in the presence of excess perchlorate. As the Ion Pac AG5A-5 μm/AS5A-5 μm column set is of older technology, future availability may be of concern.

$$2TiH_x + (1 + 0.25x)KClO_4 \Rightarrow 2TiO_2 + (1 + 0.25x)KCl + xH_2O$$

Fig. 4. Decomposition reaction of titanium or titanium subhydride with potassium perchlorate for $x = 0$–2.

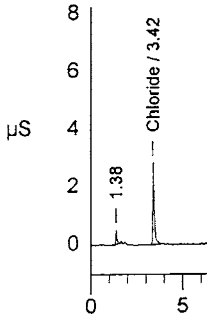

Fig. 5. Chromatogram of CP with 1 μg/ml of chloride. Ion Pac AG5A-5 μm/AS5A-5 μm.

We have also found that use of the Ion Pac AS9HC/AS9HC column set provides a good method for anion analysis of materials containing a large perchlorate matrix (5000 ppm perchlorate for dissolved samples). The AS9HC is a column that was optimized by Dionex for oxyhalides. As shown in Table 1, comparable results were obtained for chloride on the Dionex Ion Pac AG5A-5 μm/AS5A-5 μm or the Dionex Ion Pac AS9HC/AS9HC column sets for CP samples that had undergone accelerated aging in detonators.

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[2] The suppressor bypass was suggested and implemented by Robert Mickle, Dionex Corporation.

Table 1
Comparison of chloride values for samples of CP from a detonator aging study analyzed using the Ion Pac AG5A-5 μm/AS5A-5 μm and the Ion Pac AG9HC/AS9HC column sets[a]

Sample ID	AG5A-5 μm/ AS5A-5 μm	AG9HC/ AS9HC
1 Year, 50 °C	56	50
1 Year, 70 °C	47	46
1 Year, 100 °C	34	32
2 Years, ambient	47	39
2 Years, ambient	53	46
2 Years, 50 °C	37	44
2 Years, 50 °C	141	140
2 Years, 100 °C	74	68
2 Years, 100 °C	380	390
2 Years, 100 °C	430	480

[a] Results are given in μg/g.

Agreement is better than 80% between values obtained on the two different column sets from the same solution for each sample. Some of the samples were from multiple detonators that had been aged at the same conditions. Note that the replicates for the last two aging conditions do not repeat well. This lack of repeatability is easily seen using either column set and is possibly due to a difference in the hermeticity of the detonator. It is not unusual to see differences in data for different detonators aged for similar time periods.

The user of the AG9HC/AS9HC column set has the advantage of being able to resolve and analyze nitrate and chlorate as seen in the chromatogram of calibration standard shown in Fig. 6. This column set can also be easily used for the analysis of other anions such as nitrite, bromide, sulfate, and phosphate in the same run if those are also of interest. Analysis of titanium subhydride/potassium perchlorate blends has shown that the blends, as well as the starting potassium perchlorate, contain both chlorate and nitrate as shown in Table 2 and Fig. 7. Nitrate is present as a contaminant, but chlorate could be present as either a contaminant or a decomposition product. It is necessary to have accurate characterization of baseline unaged powder to be able to determine whether chlorate is present as a decomposition product over the course of a surveillance program or aging study. Cations are not usually seen on anion columns, but the large peak between 2 and 3 min seen in Fig. 7 is probably due to the large amount of potassium ion that elutes with the water in the sample.

Table 2
Chloride, chlorate, and nitrate values for blends of $TiH_{1.65}/KClO_4$ in μg/g[a]

Sample ID	Chloride	Chlorate	Nitrate
$KClO_4$ for blend A	32 (2)	147 (7)	53 (8)
Blend A	38 (14)	110 (20)	39 (4)
Blend B	115 (6)	280 (20)	40 (6)
Blend C	119 (5)	286 (4)	39 (4)

[a] The standard deviation for five samples in parentheses.

The AG9HC/AS9HC column set does have the disadvantage that only three to five samples, depending on the age of the columns can be analyzed before

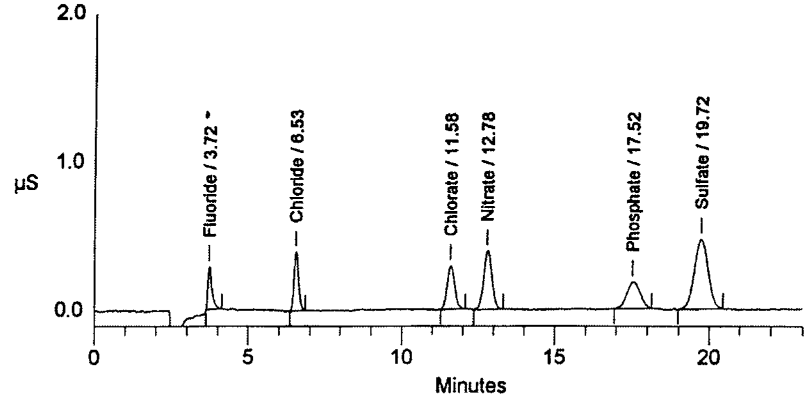

Fig. 6. Chromatogram of calibration standard run using the Ion Pac AG9HC/AS9HC column set.

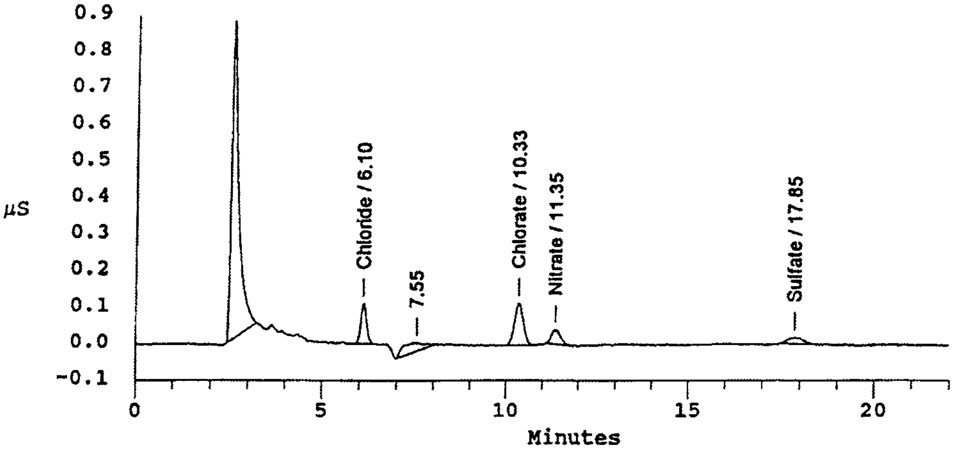

Fig. 7. Chromatogram of potassium perchlorate on an Ion Pac AG9HC/AS9HC column set.

the perchlorate anion starts to elute and interfere. The column set uses a 9 mM Na_2CO_3 eluent and is allowed to rinse with eluent for about 2 h before the next set of samples is run. With an autosampler, the rinse steps can be included in the sample schedule as the appropriate number of deionized water injections, and we use this column set as our default method for anion analyses of samples with a large perchlorate matrix. The column set remains in calibration after the rinse injections; however, calibration standards are run as samples in the autosampler schedule before the next samples for confirmation. We follow the EPA 300 guidelines of ±10% for calibration check samples, but our calibration checks are usually within ±5%. Attempts to step the eluent concentration to higher levels to elute the perchlorate faster resulted in loss of calibration. The retention times for chloride, chlorate, nitrate, and sulfate are stable through multiple rinse cycles, and area counts for these anions repeat within 90% or better. Results from recovery experiments are usually within ±10% of the expected 100%; however, columns that are near the end of life can show incomplete chloride recoveries for solutions that are ≤ 1 µg/ml. Calculated recoveries can be higher than 100% because of experimental uncertainty and difficulty in completely excluding trace contamination, especially chloride. Because the baseline of this column set is somewhat noisier than the AG5A-5 µm/AS5A-5 µm, the latter column set is recommended if solutions must be analyzed that are expected to be ≤ 0.1 µg/ml of chloride.

Chloride analysis is performed for surveillance programs to address concerns about corrosion in devices that contain either CP or titanium or titanium/subhydride blends with potassium perchlorate. An example occurred during the manufacture of a pyrotechnic device in which corrosion of the pins and bridgewire was found within 1 month of manufacture [5,6]. See Figs. 8 and 9 for examples. Powder in contact with the bridgewire and pins was found to contain more chloride than bulk powder. The corrosion was found to be chloride induced due to potassium perchlorate decomposition in the presence of moisture and organic contaminants at the bridgewire/pin interface. Aggressive cleaning and drying procedures were

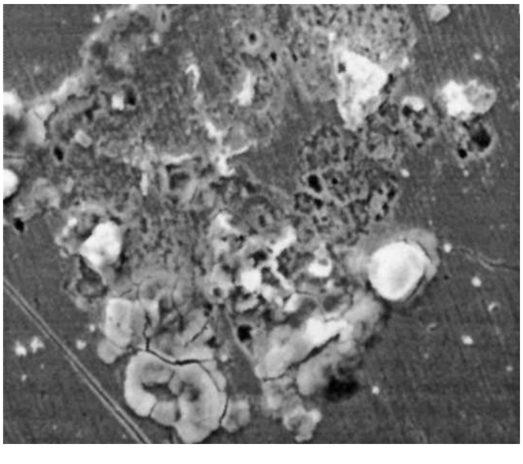

Fig. 8. Pin corrosion.

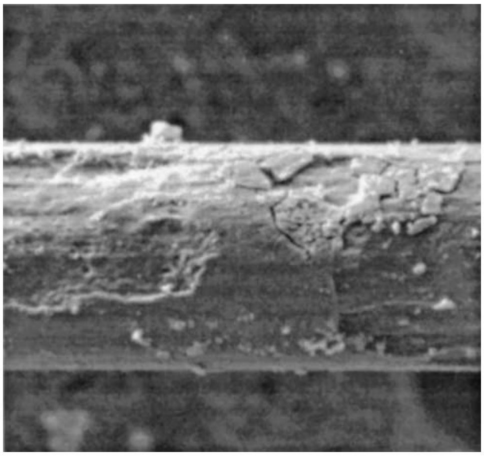

Fig. 9. Bridgewire corrosion.

introduced into the manufacturing processes and eliminated the problem. Surveillance of these devices shows that the chloride levels remain low 20 years later, and no corrosion problems have resulted.

4. Anion analysis of composite propellants containing ammonium perchlorate

Anion analysis has also been applied to composite propellants containing ammonium perchlorate with either polysulfide or hydroxyterminatedpolybutadiene (HTPB) binders. These organic polymers are not soluble in water, and so the samples are prepared by extracting the water soluble portion. We have found a Spex 8000 Mixer/Mill, as shown in Fig. 10, to be helpful in preparing samples such as these. Plastic vials and agitator balls are available as well as a fixture for preparing up to seven samples at once as shown in Fig. 11. About 200 mg of propellant shavings are extracted with 2.5–3 ml of deionized water for 15 min. The extract is removed and replaced with deionized water, and the sample is extracted again. This process is repeated until four extracts are obtained. The four extracts are combined to get >95% extraction of the ammonium perchlorate and presumably the water soluble anions. Complete extraction of the ammonium perchlorate was confirmed both by ammonium ion and gravimetric analysis. In addition to chloride, propellants with polysulfide binder can contain sulfate and thiosulfate as decomposition products. Thiosulfate moves slowly through an AG9HC/AS9HC column set and is better analyzed using an Ion Pac AG16/AS16 column set. A chromatogram of calibration standard is shown in Fig. 12. Sulfate and chloride can also be quantitated, however, sulfate and sulfite coelute in this analysis method. Therefore, the sample should also be run on the AG9HC/AS9HC column set to confirm the absence of sulfite and also to quantitate nitrate and chlorate. Sulfite does coelute with phosphate using this column set, but in our experience neither has been detected. Thiosulfate needs to be eluted before the next sample is injected to avoid interference from carryover, and so the flow rate is increased after elution of sulfate and then reequilibrated at the original flow rate before the next sample is injected. The system stays in calibration.

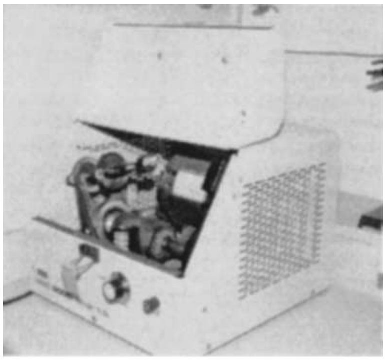

Fig. 10. Spex 8000 Mixer/Mill.

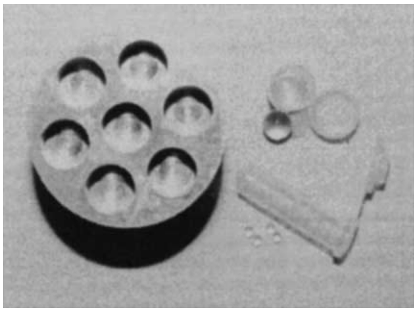

Fig. 11. Fixture for preparation of seven samples in the Spex 8000 Mixer/Mill.

HTPB propellants are not expected to produce sulfur-containing anions upon decomposition, and so their analysis is more straightforward. The main

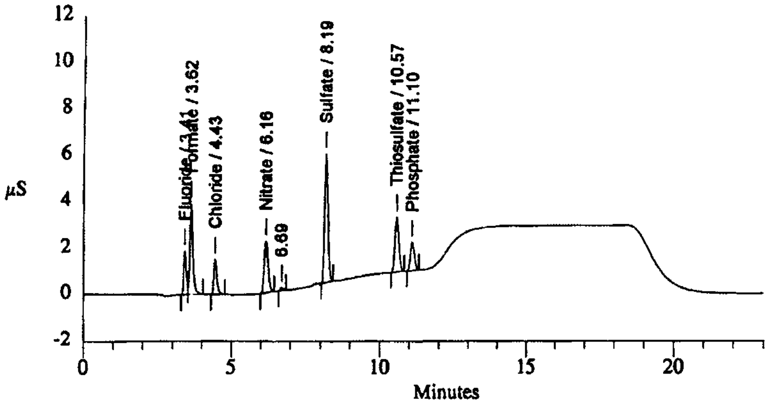

Fig. 12. Chromatogram of calibration standard including thiosulfate. The baseline shifts are due to changing eluent concentration. Ion Pac AG16/AS16.

interest is the presence of chloride ion. We have obtained good results by performing the same kind of extraction as described for propellants with polysulfide binder and analysis with the AG5A-5 µm/AS5A-5 µm column set. We have not had the occasion to try analyses of HTPB propellants using the AG9HC/AS9HC column set. Characterization of unaged baseline propellant is important because chloride can be present as a contaminant in the ammonium perchlorate used in the formulation and possibly as a decomposition product.

5. Analysis of perchlorate

The Dionex Ion Pac AG16/AS16 can also be used for the analysis of perchlorate. We are usually interested in other anions that may be present as well, and so the analysis is run with a less concentrated gradient of sodium hydroxide which is stepped to 70 mM to elute and analyze the perchlorate. A chromatogram of calibration standard is shown in Fig. 13. We have used this method to identify unknown residues as being composed of mainly ammonium perchlorate in conjunction with cation analysis of the same solution for ammonium ion. If only perchlorate is of interest, the analysis could be done with an isocratic run of 70 mM sodium hydroxide.

6. Ammonium ion analysis of CP

A study of the thermal decomposition of CP has shown that in addition to chloride, ammonium ions

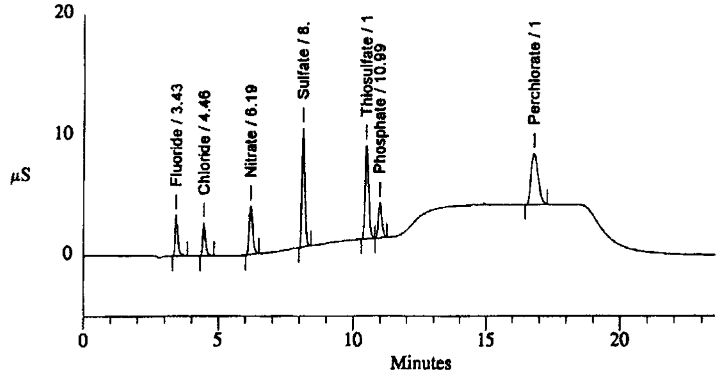

Fig. 13. Chromatogram of calibration standard including perchlorate. Ion Pac AG16/AS16.

were also present [4], and analysis of these species can be used to determine the extent of decomposition during shelf life, accelerated aging, and compatibility studies. Dissociation of the ammonia ligands and reaction to ammonium ion has been found to occur during the first stage in the decomposition of CP, whereas production of chloride occurs in the later stages [4]. Chloride is also a ubiquitous contaminant and could be present due to decomposition and/or inadvertent contamination during processing and manufacturing operations (Contamination during sample preparation can be discovered by preparing blanks along with the samples). For these reasons ammonium ion is a better indicator of decomposition than chloride in CP samples for surveillance purposes and for samples that have not been severely aged. Data from long term, severely aged samples of CP have shown the extent of decomposition to be similar when based on either ammonium or chloride ion data. Determination of ammonium ion concentration can be accomplished using an Ion Pac CG12A/CS12A guard/analytical column set with 20 mM methanesulfonic acid as the eluent. A sample chromatogram is shown in Fig. 14. Five samples can be run before a broad "peak" elutes that is characteristic of CP. Two to three hours are then required to stabilize the baseline again before more samples can be analyzed. A reduction in the retention time for ammonium ion is noticed with each successive injection, but it is only a few hundredths of a minute. Ammonium ion area counts for the five injections repeat within 95% for the same solution of CP. The system remains in calibration after the rinse.

7. Analysis of smoke composition

Many energetic material samples can be prepared by either dissolving in or extracting with deionized water. Some, however, require other treatment. One example is a smoke composition that contains potassium chlorate and terephthalic acid. Potassium chlorate is soluble in water, but terephthalic acid (TPA) is not. It was of interest to determine if the concentrations of chlorate and TPA were decreasing with age in an accelerated aging experiment at 70 °C. The analysis had to include chloride as well because it is a probable decomposition product of chlorate. TPA would have to be analyzed as a salt, and so experiments were done to determine its solubility in dilute sodium hydroxide solutions. Drill turnings of smoke composition were extracted twice with 50 mM sodium hydroxide with 10% methanol. The extracts were combined, filtered, and run on a Dionex Ion Pac AG11/AS11 column set. A chromatogram of the calibration standard is shown in Fig. 15.

Samples were run undiluted to obtain the chloride data and then diluted to obtain the TPA data. Chlorate was determined using a Dionex Ion Pac AG12/AS12 column set, which is similar to the AG9HC/AS9HC set, and thus allows the resolution of nitrate and chlorate. Chloride showed a five-fold increase over the span of the accelerated aging study. Chlorate and TPA results are shown in Fig. 16. Three determinations were made at each point (except five for baseline), and within the accuracy of the data, it does not appear that either chlorate or TPA is showing measurable loss over time.

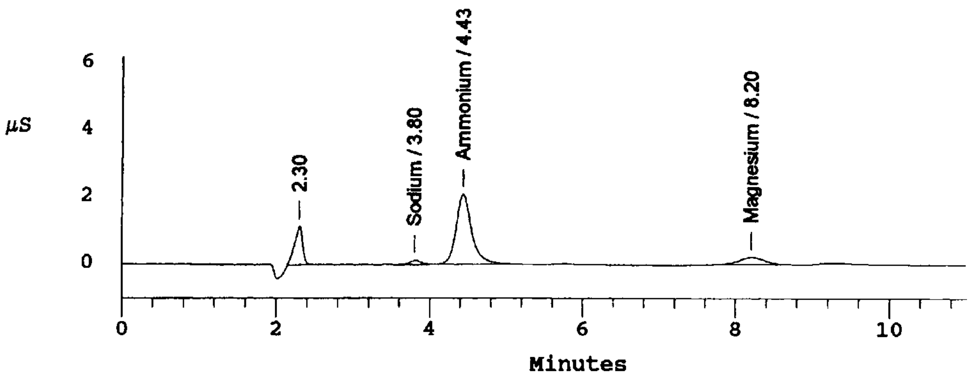

Fig. 14. Chromatogram of ammonium ion in CP. Ion Pac CG12/CS12.

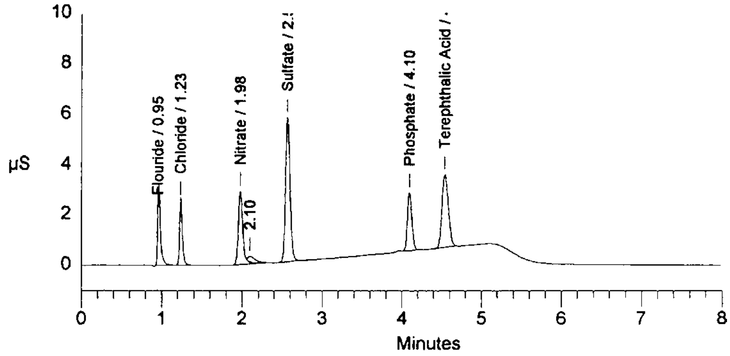

Fig. 15. Chromatogram of calibration standard showing standard anions and terephthalic acid. Baseline shifts are due to changes in eluent concentration. Ion Pac AG11/As11.

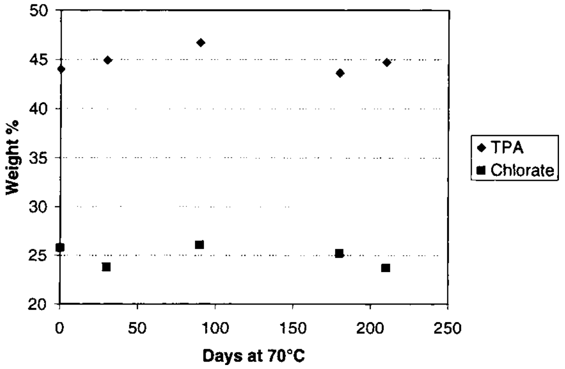

Fig. 16. Days stored at 70 °C vs. chlorate and TPA wt.%.

IC is best used to determine trace quantities and is somewhat limited if precise determinations of composition are needed. At best, one cannot expect better than ±2–3%. This kind of precision may not be adequate for determination of composition, but is usually acceptable for trace quantities. In this case the standard deviations for each data point in the graph ranged from 0.1 to 3.8. Variability was also probably seen because the sample had to be extracted from an organic matrix. As one might expect, the samples of highest surface area gave the most consistent results.

8. Analysis of primer mix

We have also analyzed a primer mix that contains lead thiocyanate as the fuel and potassium chlorate as the oxidizer. Lead thiocyanate is not soluble in water, and so the sample was dissolved in 100 mN acetic acid, filtered, and run on the Dionex Ion Pac AG16/AS16 column set for thiocyanate. A chromatogram is shown in Fig. 17. Although chlorate can be determined on this column, resolution from nitrate remains a challenge and so chlorate determinations were done with the AG9HC/AS9HC column set to be sure nitrate was not interfering.

9. Analysis of organic explosives

Ion chromatography can also be applied to organic explosives, such as pentaerythritoltetranitrate (PETN), hexanitrostilbene (HNS), and octogen (HMX). The sample is extracted rather than dissolved. The results can be used for evidence of ionic processing contamination, reaction products, or PETN decomposition. Samples are processed in a plastic vial containing a plastic agitator ball with deionized water in a Spex 8000 Mixer/Mill as described previously for composite propellants except that in this case, the goal is to pulverize and disperse the sample. This mechanical extraction appears to be better than extraction using sonication in that the mechanical extraction pulverizes and disperses the sample better and gives more consistent analytical results. Particle size is not normally determined during sample preparation; however, in one experiment sonication of PETN in water reduced the mean particle size from 14 to 11 µm, whereas mechanical extraction by pulverizing the sample in

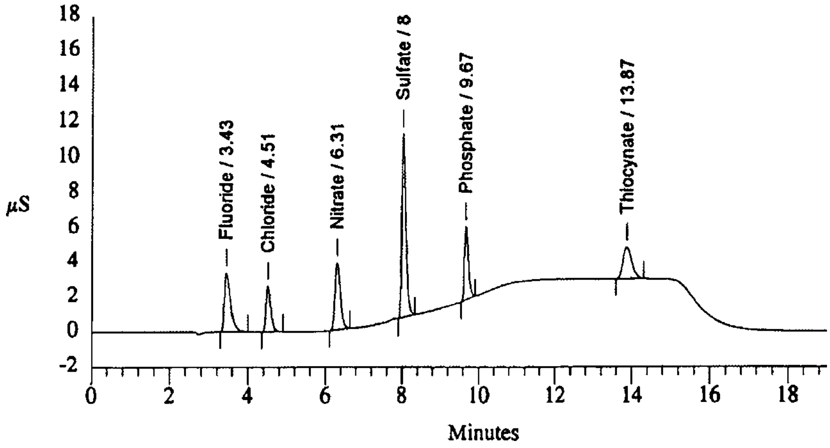

Fig. 17. Chromatogram of calibration standard plus thiocyanate. The baseline shifts are due to change in eluent concentration. Ion Pac AG16/AS16.

water reduced the same starting PETN to 8 µm. Sonication also appears to increase the presence of ionic species. Nitrite is often detected in sonicated PETN but not in PETN prepared in a mixer mill. Nitrate values can be higher in sonicated PETN than in comparable PETN extracted in a mixer mill. In addition, the repeatability of nitrate and nitrite values in replicates that are sonicated can be poor. It depends on the kind of PETN being analyzed. Not all PETN materials act alike with respect to ion analysis. If chloride is present, both sonication and mixer mill preparation methods will extract chloride equally well. Presumably sonication may be inducing variable levels of decomposition in PETN, and thus our samples are prepared using mixer mill extraction only.

In examining PETN from a variety of sources and aging programs, the following ionic decomposition products were found: nitrate, acetate, formate, and oxalate. Oxalate is perhaps the most surprising of these and could also be present in starting material as a contaminant from the synthesis process. The majority of the bulk unaged PETN powders that we have examined are clean, however, and do not contain oxalate or appreciable amounts of other anions as contaminants. After experiencing specific environments, ionic evidence of decomposition can be seen. An example is shown in Fig. 18 where PETN was stored 1 year at 100 °C and was compared to that same PETN stored at ambient temperature. The levels of ionic decomposition products are rarely high enough to cause a problem in and of themselves, but they can be symptomatic of other reactions that may indeed be a problem such as an incompatibility.

In a final example, ion chromatography has also been used to determine ionic products of thermally aged XTX8003, which is an extrudable explosive composed of 80% PETN and 20% Sylgard 182 [7]. Sylgard microencapsulates the PETN during processing. XTX8003 is a rubbery material and does not pulverize. The challenge was to efficiently extract PETN and all associated ionic material. Results of a screening study are shown in Table 3. Analysis of PETN that was used to formulate XTX8003 showed

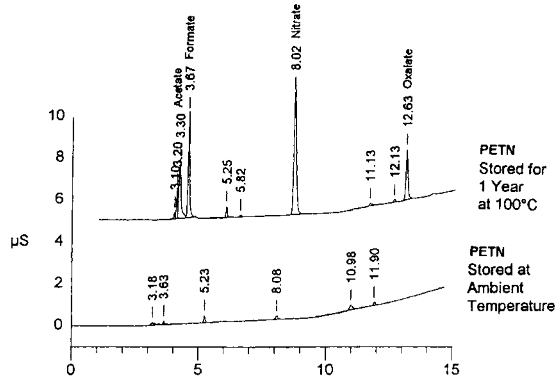

Fig. 18. Chromatograms of aged and unaged PETN. Ion Pac AG11/AS11.

Table 3
Screening study to determine a solvent for extraction of XTX8003 for ion analysis

	Acetonitrile		Methanol		Acetonitrile:methanol (vol.%) 50:50	
	XTX8003	PETN	XTX8003	PETN	XTX8003	PETN
Extracted (%)	76	97	28	31	79	99.5
Chloride (μg/g)	<3	6.8	<3	89	<3	87
Nitrate (μg/g)	<9	64	<9	85	<9	84

a clean material and so to be sure ionic species were being extracted as well, the screening studies were also done on PETN powder that was known to contain 85–90 μg/g each of chloride and nitrate as contaminants. As the data in the table show, acetonitrile is fairly efficient at extracting PETN, but not ionic species, and methanol is fairly efficient at extracting ionic species, but not PETN. Both objectives could be met by using 50:50 acetonitrile:methanol. The extraction was done using the Spex Mixer/Mill with the sample and solvent contained in a polypropylene snap cap centrifuge tube. Samples of 20 mg were extracted twice with 750 μl of solvent each time. Thinner samples could be extracted efficiently at room temperature in the mixer mill, but for thicker samples, treatment for a few hours in a water bath at 50 °C was needed prior to the mixer mill step for efficient extraction. The solvents were allowed to evaporate leaving a PETN residue that could then be prepared for ion chromatography by extraction with deionized water.

TX8003 samples that had been stored at 50, 70, and 90 °C for periods of time up through 2 years were analyzed. All four of the expected ionic decomposition products were found, but their combined total did not even reach 250 μg/g for any of the aged samples. When the PETN that is used to formulate XTX8003 was aged without binder, the acetate levels reached 350–500 μg/g after 12–24 months of aging at 90 °C. Similarly aged XTX8003, however, only shows acetate levels of 15 μg/g, suggesting that the Sylgard binder has a protective effect with respect to ionic decomposition.

The range of energetic materials that can be subjected to analysis using ion chromatography is undoubtedly broader than that presented in this paper, but this information is offered to illustrate some of the applications we have made in energetic materials analysis and also some of the challenges we have faced. We hope that our solutions to these problems will be helpful to the community of energetic materials analysts.

Appendix A. Sample preparation and method details to supplement the text

Sample	Sample preparation	Column set[a]	Eluent	Isocratic/gradient	Flow rate (ml/min)
$TiH_x/KClO_4$, ($x = 0$–2) chloride, chlorate, nitrate, and sulfate ions	Dissolve 10 mg in 1000 µl of deionized water (only the $KClO_4$ will dissolve). Filter through a 0.45 µm ion chromatography syringe filter	AG9HC/AS9HC	9 mM Na_2CO_3	Isocratic: three–five samples can be run before the column must be rinsed with 4–5 deionized water injections	1.0
CP chloride, chlorate, nitrate, and sulfate ions	Dissolve 10 mg in 1000 µl of deionized water. Filter through a 0.45 µm ion chromatography syringe filter	AG9HC/AS9HC	9 mM Na_2CO_3	Isocratic: three–five samples can be run before the column must be rinsed with 4–5 deionized water injections	1.0
CP ammonium ion	Dissolve 10 mg in 1000 µl of deionized water. Filter through a 0.45 µm ion chromatography syringe filter	CG12A/CS12A	20 mM methane-sulfonic acid	Isocratic: five samples can be run before the column must be rinsed with 7–8 deionized water injections	1.0
Composite propellant (AP) polysulfide binder	Thin shavings of propellant (200 mg) are extracted with deionized water (2.5–3 ml) in a 4.0 ml Spex vial with a 3/8″ agitator ball for 15 min. The process is repeated a total of four times with fresh deionized water each time. The extracts are combined and brought to a volume of 50 ml in a class A volumetric flask	AG16/AS16 for thiosulfate and sulfate	NaOH	Gradient: 15–70 mM	1.0
		AG9HC/AS9HC for confirmation that no sulfite is present and resolution of nitrate and chlorate	9 mM Na_2CO_3	Isocratic: after elution of sulfate the flow rate is increased from 1.0 to 1.5 ml/min for 64 min to elute thiosulfate. The system is then reequilibrated at 1.0 ml/min for 8 min to give a total run time of 95 min	1.0, 1.5, 1.0
Composite propellant (AP) HTPB binder	Similar to composite propellant (AP) polysulfide binder	AG5A-5 µm/ AS5A-5 µm	NaOH	Gradient: 15–30 mM then step to 200 mM to elute perchlorate (suppressor bypass)	1.0
Smoke composition	Powdered smoke composition (9–9.5 mg) was extracted with 1500 µl of 10% methanol in 50 mM NaOH in a Spex Mixer/Mill for 10 min after a 10 min wait. The extraction is repeated for 10 min after another 10 min wait. Filter through a 0.45 µm ion chromatography syringe filter	AG11/AS11	NaOH	Gradient: 10–30 mM	2.0
Primer mix	8–14 mg were dissolved in 1 ml of 100 mN acetic acid with 1 min sonication, and then diluted to 25 ml in a class A volumetric flask	AG16/AS16 for thiocyanate	NaOH	Gradient: 15–70 mM	1.0
		AG9HC/AS9HC for chloride and chlorate	9 mm Na_2CO_3	Isocratic: three samples can be run before the column must be rinsed (four injections of DI water) to remove thiocyanate	1.0
PETN	20 mg were extracted with 1500 µl of deionized water in a 2 ml Spex Mixer/Mill vial with a 3/8″ agitator ball for 10 min after a 10 min wait. The extraction is repeated for 10 min after another 10 min wait. Filter through a 0.45 µm ion chromatography syringe filter	AG11/AS11	NaOH	Gradient: 0.25–20 mM	2.0

[a] All column sets are Dionex Ion Pac.

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