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TECHNICAL NOTE

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The Analysis of Black Powder Substitutes Containing Ascorbic Acid by Ion Chromatography/Mass Spectrometry*†

ABSTRACT: Black powder substitutes containing ascorbic acid are a group of low explosives that utilize ascorbic acid as the fuel. The analysis of these powders is complicated by the degradation of ascorbic acid which occurs rapidly in solution and may also occur as the powder ages. Aqueous extracts of both intact powders and postblast residues were analyzed by an existing ion chromatography/mass spectrometry (IC/MS) method used at the Bureau of Alcohol, Tobacco, Firearms and Explosives. Results have shown that while ascorbic acid itself is not detected in this method, its diagnostic degradation products (threonic acid, monohydrated diketogulonic acid, and oxalic acid) can be identified. In addition, anions from the inorganic oxidizers (perchlorate and nitrate) and combustion products such as chloride, chlorate, and nitrite, can be identified within the same experiment. While this IC/MS method shows promise, future modifications are necessary because of limitations in identifying threonate in postblast residues, as well as coeluting compounds observed in postblast residues.

KEYWORDS: forensic science, explosives, ascorbic acid, black powder substitutes, ion chromatography-mass spectrometry, postblast residues

Black powder substitutes have been gradually taking the place of traditional black powder on retail shelves since the introduction of Hodgdon Pyrodex in the 1970s. Since they are classified as flammable solids (1,2), black powder substitutes do not have the same restrictive storage requirements as traditional black powder (1), which makes them more appealing to retailers. In fact, during the course of this study, we discovered that some local sporting stores like Bass Pro Shops and Atlantic Guns Incorporated, have stopped carrying traditional black powder altogether in favor of various black powder substitutes.

Over the years, many sulfur-free powders such as Triple Seven (Hodgdon Powder Company, Shawnee Mission, KS) and Clear Shot (GOEX, Incorporated, Doyline, LA) have been introduced, promising less fouling and easier clean-up of muzzle-loaded weapons. The current trend among black powder substitutes is the utilization of organic acids as a replacement fuel for sulfur. Ascorbic acid, commonly known as vitamin C, is one such organic acid that is currently being used in several black powder substitute formulations. The first of these ascorbic acid-containing powders, Golden Powder, was patented in 1985 (1) but was never produced commercially. Table 1 summarizes the various ascorbic acid-containing powders produced over the years (1,3). Clean Shot, which is no longer under production, was reintroduced later as American Pioneer Powder.

According to data collected between 2002 and 2007 by the Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF) Bomb Data Center, low explosives, such as black powder, black powder substitutes, and smokeless powder, continue to be the explosive of choice for many bombers in the United States. While Hodgdon Pyrodex is the most commonly encountered black powder substitute in ATF casework, ascorbic acid-containing powders are starting to appear more often. Consequently, a sensitive analytical method is needed for identifying trace amounts and postblast residues of these ascorbic acid-containing propellants.

Ascorbic acid has been extensively studied in various fields such as food science, biochemistry, and analytical chemistry (4–14). Ascorbic acid degrades under several conditions, such as exposure to light, heat, metal ions, and when dissolved in aqueous media (7,8,11). The rapid degradation of ascorbic acid in solution is a well-documented phenomenon, and can result in over 50 different degradation products, depending on the conditions (6–8). The initial degradation pathway, however, has been established as follows: the ascorbic acid is first reversibly oxidized to dehydroascorbic acid, which then degrades further to 2,3-diketogulonic acid in an irreversible reaction (1,10,11). In one of the reaction pathways illustrated in Goodpaster and Keto's paper (1) seen in Fig. 1, the 2,3-diketogulonic acid further degrades to threonic acid (L-threonate or 2,3,4-trihydroxybutanoic acid) and oxalic acid (1,2-ethanedioic acid). However, dehydroascorbic acid can also undergo rapid rehydration as Fig. 2 depicts, followed by spontaneous hydrolysis at the lactonic ring to produce the diketogulonate anion in its monohydrated (m/z = 209) and/or dihydrated (m/z = 227) form(s) (11).

The rapid degradation of ascorbic acid complicates the identification of these black powder substitutes, especially in postblast

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TABLE 1—*Summary of black powder substitutes containing ascorbic acid (AA).*

	Main Ingredients	Manufacturer/Marketer	Comment
Golden Powder	KNO_3, AA	Golden Powder Company	Patented in 1985
Black Canyon Powder	KNO_3, AA	Legend Products Corp., Las Vegas, Nevada	Manufactured *c.* 1994–1996
Black Mag or Arco-Black Mag	KNO_3, $KClO_4$, AA	Arco Powder Company of Hollywood, Florida	First appeared in *Guns and Ammo* magazine, January 1996
Clean Shot	KNO_3, $KClO_4$, AA	Clean Shot Technologies of Whitewater, Colorado	First appeared in *Handloader* magazine, February–March 1999
American Pioneer Powder	KNO_3, $KClO_4$, AA	American Pioneer Powder, Inc., of Whitewater, Colorado	Introduced *c.* 2002
Pinnacle Replica Powder	KNO_3, $KClO_4$, AA	GOEX, Inc., Doyline, Louisiana	Introduced in 2004
Jim Shockey's Gold	KNO_3, $KClO_4$, AA	American Pioneer Powder, Inc., of Whitewater, Colorado	Introduced in 2005
Black Mag 3	KNO_3, $KClO_4$, AA	Arco Powder Company of Hollywood, Florida	Black Mag or Arco-Black Mag was re-released as Black Mag 3 in 2006

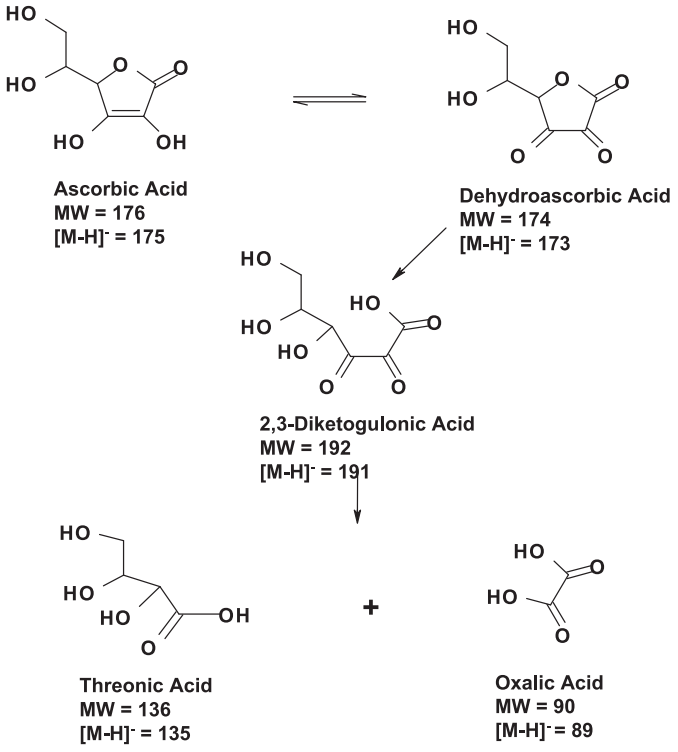

FIG. 1—*One of the degradation pathways of ascorbic acid, as illustrated by Goodpaster and Keto (1).*

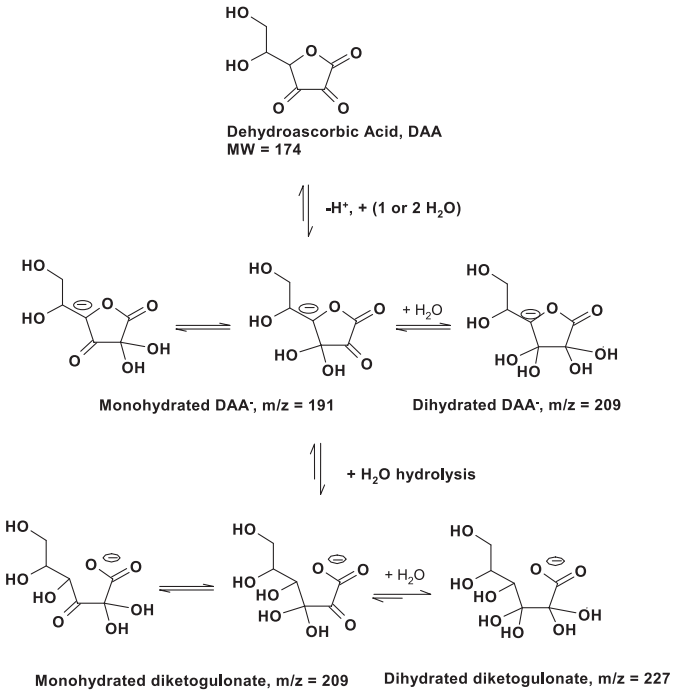

FIG. 2—*Formation of monohydrated diketogulonate, m/z = 209, as described by Cioffi et al. (11).*

devices. Bulk analytical techniques, such as X-ray diffraction (XRD), have been successful in identifying ascorbic acid in intact and well-preserved powders (2). However, in a postblast device, without significant amounts of unreacted powder, traditional bulk methods of analysis fail to identify the original ascorbic acid fuel. Recent studies of these powders have used more sensitive analytical techniques such as liquid chromatography–mass spectrometry (LC–MS) (15,16), gas chromatography–mass spectrometry (GC–MS) (1), and ion chromatography (IC) and capillary zone electrophoresis (CE) (M. Bottegal, personal communication; Pittsburgh, PA, 2006). The GC–MS method requires derivatization of ascorbic acid with trimethysilyl reagents, while in the IC and CE methods described by Bottegal, cysteine was added to slow the degradation of ascorbic acid. Although the LC–MS, GC–MS, IC, and CE methods have been successful in identifying ascorbic acid and/or its degradation products in intact powders, a method sensitive enough to identify ascorbic acid in postblast residue has yet to be reported. This paper will explore the use of IC/MS in the analysis of both intact and postblast ascorbic acid black powder substitutes.

Materials and Methods

American Pioneer Powder, Goex Pinnacle Replica Black Powder, Jim Shockey's Gold, and Clean Shot, were purchased from local sporting goods shops and a sample of Black Mag 3 was received from Megan Bottegal of Florida International University. These powders, in addition to laboratory exemplars of Golden Powder and Black Canyon Powder, were included in the intact powder research. L-(+)-ascorbic acid (J.T. Baker, Phillipsburg, NJ), dehydroascorbic acid (Sigma-Aldrich, St. Louis, MO), L-threonic acid, calcium salt (TCI America, Portland, OR), and oxalic acid (Midwest Consultants, Inc., St. Louis, MO) were acquired from chemical supply companies. Deionized (DI) water (18-megohm) was obtained using a Millipore Milli-Q water purification system (Bedford, MA). Water extracts were filtered with 25 mm IC

Acrodisc® syringe filters with a 0.45 μm Supor® polyethersulfone (PES) membrane (Pall Life Sciences, Ann Arbor, MI).

To obtain postblast residues, six pipe bombs were constructed and filled with either Goex Pinnacle Replica Black Powder or Jim Shockey's Gold. Four pipe bombs were constructed with a 1-inch nominal diameter by 8-inch galvanized steel pipe with two galvanized iron end caps. These devices were initiated by a length of black powder pyrotechnic fuse and an electric match (double-primed). Two additional pipe bombs were constructed with a 1 -inch nominal diameter by 5-inch galvanized steel pipe, with two galvanized iron end caps. These devices were initiated with an electric match only (single-primed). Each device was filled *c.* ¾-full with the explosive powder. Both powders (Pinnacle and Jim Shockey's Gold) were tested three times (twice in the double-primed 1 × 8-inch devices and once in the 1 × 5-inch single-primed device) for a total of six devices. There was insufficient quantity of the other powders for postblast testing.

Sample Preparation

The ascorbic acid, dehydroascorbic acid, threonic acid, and oxalic acid standards were prepared by dissolving a small amount of each in DI water to give a conductivity reading of *c.* 20 μS (micro-Siemens). The ascorbic acid standard had a pH of 4.1, and the laboratory DI water was slightly acidic, with a pH of 5.85. Extracts of the intact explosives were prepared by dissolving two FFg particles in *c.* 4 mL DI water. Extracts of postblast residues were prepared by rinsing the interior surface of pipe or end cap fragments with DI water. All water extracts were then filtered using the 25 mm IC Acrodisc® syringe filters, and diluted as needed.

Instrumentation

The IC/MS system consisted of a DIONEX DX-500 ion chromatograph and a Thermo Finnigan MSQ single quadrupole mass spectrometer equipped with enhanced low mass option (ELMO). The DX-500 system consisted of the following DIONEX components: GS-50 pump, CD-20 conductivity detector, LC-30 chromatography oven, and an EG-40 eluent generator with a KOH cartridge. An AS-40 automated sampler and a 10-μL external sample loop were used for sample injections. A 2-mm ASRS MS anion self-regenerating suppressor was operated in external water mode at a current of 100 mA.

A 2 × 250 mm DIONEX Ion Pac AS18 analytical column with a 2 × 50 mm DIONEX Ion Pac AG18 guard column was used to analyze the ascorbic acid degradation products and additional anions. A 23 mM KOH eluent was run at a flow rate of 0.25 mL/min for this anion method. A 2 × 250 mm DIONEX Ion Pac AS16 analytical column with a 2 × 50 mm DIONEX Ion Pac AG16 guard column was used to analyze perchlorate. A 50 mM KOH eluent was run at a flow rate of 0.30 mL/min for this perchlorate method. Both methods utilized a DIONEX CR-ATC trap column and were run under isocratic conditions at 30°C.

The MSQ was run in negative electrospray ionization (ESI) mode, with a probe temperature of 400°C for the anion method and 450°C for the perchlorate method. A cone voltage of 80 V and a mass range of 30–310 amu were used for most of the anion experiments in this study, while a cone voltage of 80 V and a mass range of 40–170 amu were used for the perchlorate experiments. The scan time was set to 1.0 sec for all experiments.

A Horiba Twin Cond digital conductivity meter was used to check concentrations of water extracts prior to analysis. A Fisher Scientific brand digital pH/conductivity meter was used to measure pH values.

Results and Discussion

Ascorbic Acid Standard

Ascorbic acid is unstable in solution and degrades rapidly to form numerous compounds as previously discussed. In the degradation pathway seen in Fig. 1, ascorbic acid first converts reversibly to dehydroascorbic acid, then irreversibly to 2,3-diketogulonic acid, which then degrades further to threonic acid and oxalic acid. The ascorbic acid standard analyzed in this study appears to follow this pathway. Further investigation showed that the basic conditions of the hydroxide eluent greatly accelerated this degradation process. The IC/MS data shows that a freshly prepared ascorbic acid standard degrades to three major compounds as seen in the chromatogram in Fig. 3*a*. Peak 1 was identified as threonate and its mass spectrum is shown in Fig. 3*b*. Figure 3*c* shows the mass spectrum of peak 2, which is proposed to be 2,3-diketogulonate, but in its monohydrated form. The formation pathway of monohydrated diketogulonate is illustrated in Fig. 2. Peak 4 was identified as oxalate and its corresponding mass spectrum is shown in Fig. 3*d*. A minor peak 3 appears as a left shoulder on the oxalate peak, but was not identified.

Threonic Acid

The molecular weight (MW) of threonic acid ($C_4H_8O_5$) is 136. In Fig. 3*b*, the base peak at m/z 135 corresponds to threonate anion, $[M\text{-}H]^-$, while a small peak at m/z 271 corresponds to the dimer. The mass spectrum suggests that threonate fragments between C_2 and C_3 to give m/z 75, corresponding to the $C_2H_3O_3^-$ ion. To enhance specificity, the electrospray cone voltage was decreased and as expected, the relative intensity of the dimer increased. However, when the cone voltage was dropped below 50, the m/z 75 fragment disappeared, with only m/z 135 and 271 present. An as yet unidentified m/z 279 peak was observed in the threonate mass spectrum in the ascorbic acid standard as shown in Fig. 3*b*. The IC/MS data of the threonic acid standard showed that the m/z 279 peak was missing from a freshly prepared solution, but was observed in a 1-month-old threonic acid solution.

Monohydrated Diketogulonic Acid

There was a relatively low concentration of the monohydrated diketogulonate in comparison to the other degradation products in the ascorbic acid standard, as seen in the ion chromatogram in Fig. 3*a*. Its mass spectrum in Fig. 3*c* shows a relatively complex fragmentation pattern with m/z 209 being the $[M\text{-}H]^-$ ion. The remaining peaks in the mass spectrum are interpreted as follows: a loss of 44 Da ($-CO_2$) gives the base peak of m/z 165. The m/z 147 and m/z 129 result from the sequential losses of two H_2O molecules from m/z 165. The m/z 119 is the result of m/z 147 losing a −CO group, while the m/z 101 may result from m/z 129 losing a −CO group or m/z 119 losing a H_2O. The peak at m/z 87 is 14 Da lower than m/z 101, which could correspond to CH_2. The m/z 75 is not easily explained, but may result from a loss of 44 Da from the m/z 119, which could correspond to CO_2.

When the electrospray cone voltage was lowered to 50 V, the smaller m/z 87 and 75 ions disappeared. However, when the cone voltage dropped below 40 V, the fragmentation pattern completely changed as shown in Fig. 4. The $[M\text{-}H]^-$ ion, m/z 209, now dominates the spectrum, and new ions (m/z 113, 104, and 122) start to appear. These new fragments cannot be clearly explained, but future research with MS/MS techniques may elucidate this formation pathway. The dimer, m/z 419, was observed at low

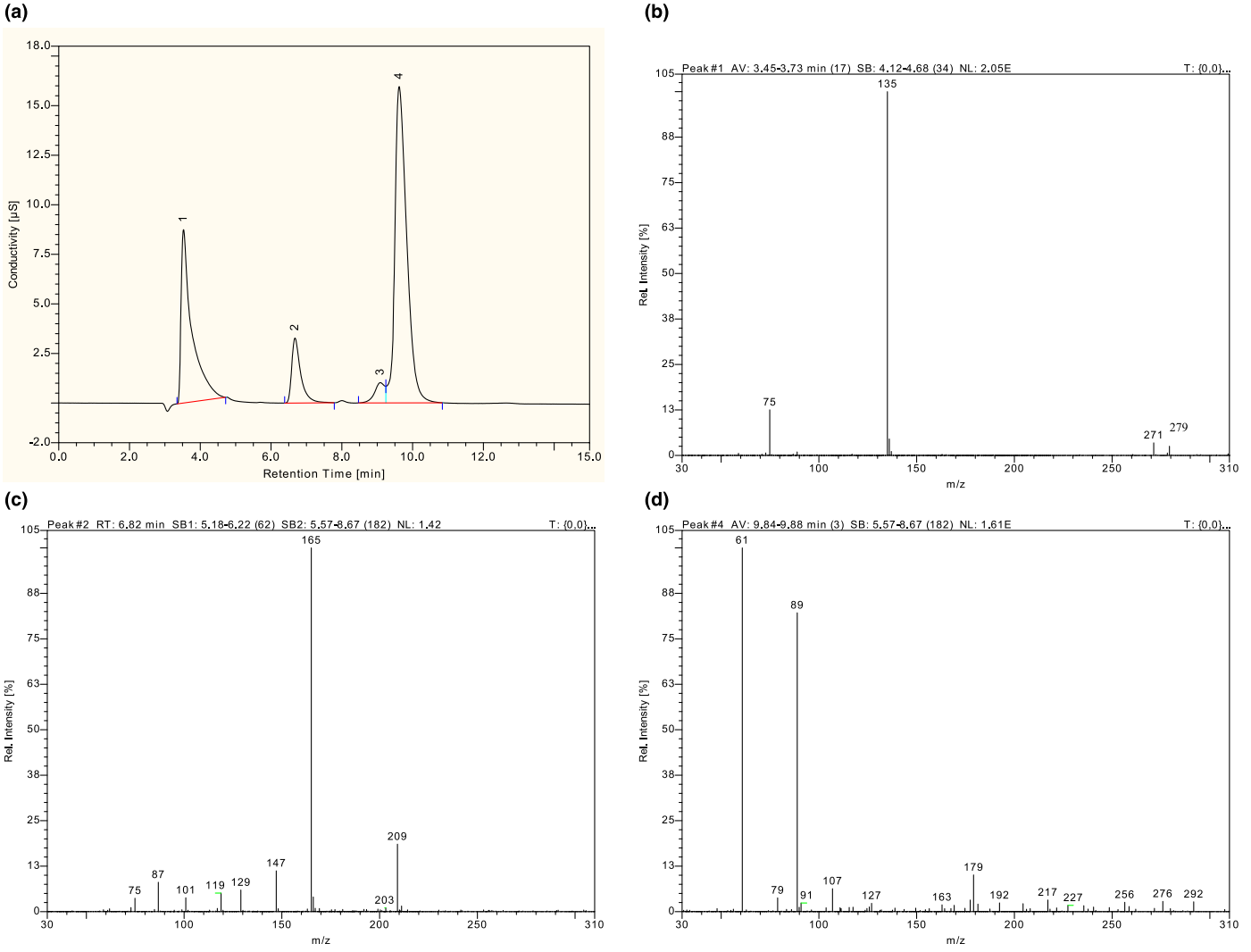

FIG. 3—*(a) Chromatogram of a fresh ascorbic acid standard: 1 = threonate, 2 = monohydrated diketogulonate, 3 = unidentified, 4 = oxalate; (b) mass spectrum of threonate (peak 1); (c) mass spectrum of monohydrated diketogulonate (peak 2); (d) mass spectrum of oxalate (peak 4).*

electrospray cone voltages such as 20 V when the mass spectrometer was scanned from 30 to 420 amu.

Oxalic Acid

Oxalic acid has a simple mass spectrum as seen in Fig. 3*d*. The m/z 89 is oxalate, the $[M\text{-}H]^-$ ion. A proposed loss of −CO results in the formation of the bicarbonate anion (HCO_3^-), m/z 61, as reported by O'Hair et al. (17). Figure 3*a* shows that oxalate is the most abundant degradation product in the ion chromatogram of the ascorbic acid standard. However, its corresponding mass spectrum is relatively weak with high background noise as seen in Fig. 3*d*. At lower electrospray cone voltages, the mass spectrometer shows a marked improvement in sensitivity for oxalate, with m/z 89 now dominating the spectrum as illustrated in Fig. 5. When the cone voltage is dropped to 50 V, the dimer of oxalic acid, m/z 179, starts to appear.

Stability of Ascorbic Acid Solution

The ascorbic acid solution was stored in a 4-mL glass vial at room temperature in the laboratory. A portion of the solution was withdrawn for analysis periodically. The data show that the concentrations of all three degradation products decreased over time with oxalate decreasing to approximately half of its original intensity in the fresh solution. The monohydrated diketogulonate peak decreased only slightly in intensity, even after 1 month. Threonate became more difficult to analyze as the solution aged because of the formation of additional ascorbic acid degradation compounds, which eluted near the threonate peak. When the solution was analyzed after only a few days, the threonate peak had broadened as a result of these coeluting compound(s). M/z 165 and 105 ions were present in this group of unresolved peaks and clearly originate from the ascorbic acid degradation cascade. An additional compound was observed at 4.5 min, with a m/z 163 base peak and a m/z 103 fragment ion. The compound(s) containing m/z 165 and 163 increased in intensity as the solution aged.

Intact Ascorbic Acid Black Powder Substitutes

Analysis of the intact ascorbic acid black powder substitutes showed a similar anion profile for all the powders, with the exception of Golden Powder and Black Canyon Powder, which will be discussed later. This profile consisted of the following anions:

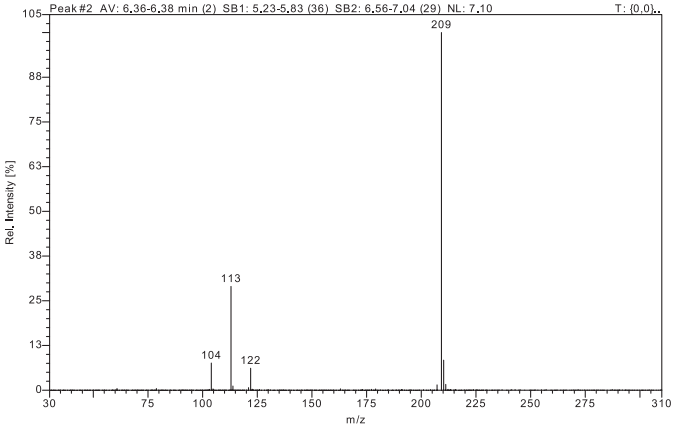

FIG. 4—*Mass spectrum of the second peak, monohydrated diketogulonate, in the ascorbic acid standard at 20 V.*

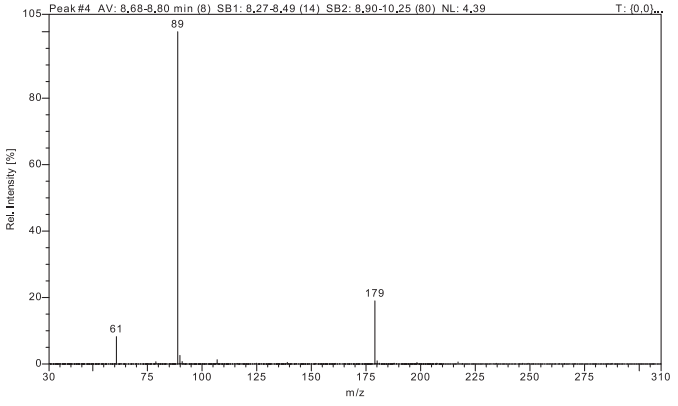

FIG. 5—*Mass spectra of oxalate at cone voltage = 40 V.*

ClO_4^-, NO_3^-, oxalate, monohydrated diketogulonate, threonate, and/or ascorbic acid degradation compounds coeluting with threonate. Figure 6*a,c* is the ion chromatograms of Jim Shockey's Gold run with the anion and perchlorate methods, respectively. In Fig. 6*a*, peak 1 is threonate, peak 2 corresponds to monohydrated diketogulonate (m/z 209), and peak 4 is oxalate. Peak 3, the largest peak in the chromatogram, is nitrate (NO_3^-), from the original oxidizer, potassium nitrate. The corresponding mass spectrum of each anion is shown in Fig. 6*b*. The threonate spectrum shows the dimer at m/z 271, $[M\text{-}H]^-$ ion at m/z 135, and a fragment ion at m/z 75. An unidentified peak at m/z 279 is also observed. The peak at m/z 105 originates from an unidentified degradation product of ascorbic acid which elutes as a right shoulder on the threonate peak. The mass spectra of the monohydrated diketogulonate and oxalate anions were consistent with those seen in the ascorbic acid standard. Their fragmentation patterns were discussed previously in the ascorbic acid standard section of this paper. The mass spectrum of nitrate consists of the molecular anion at m/z 62, and m/z 46 from the loss of an oxygen. In Fig. 6*c* (the chromatogram obtained from the perchlorate method), peaks 1 and 2 contain the unresolved anions which are separated in the anion method, and peak 3 is perchlorate, whose mass spectrum is shown in Fig. 6*d*. The fragmentation pattern of perchlorate is simple and consists of the molecular anion at m/z 99 and its Cl^{37} isotopic peak at m/z 101. The peak at m/z 83 results from the loss of one oxygen.

Other than the lack of perchlorate (Golden Powder and Black Canyon do not contain potassium perchlorate in their formulations), Golden Powder's ion profile matched that of the other intact powders. Like the other powders, Black Canyon had a strong nitrate peak, but a large difference in the ascorbic acid degradation products was observed. The oxalate peak in the Black Canyon sample was very weak, and because of the mass spectrometer's poor sensitivity for oxalate at a cone voltage of 80 V, it could not be identified. However, running the sample at a lower cone voltage should allow for easy identification of the oxalate. Monohydrated diketogulonate was not observed in the Black Canyon sample. Although coeluting compound(s) prevented the identification of threonate, the presence of m/z 165 and 105, which were seen in the month-old ascorbic acid standard solutions, are diagnostic of ascorbic acid's original presence. The Black Canyon sample was *c.* 10 years old and had been stored in a glass vial in the laboratory. Elemental analysis of Black Canyon reveals the presence of iron, which is known to accelerate the degradation of ascorbic acid (8,11). This explains the atypical response for the ascorbic acid degradation products, as compared to the other intact powders.

Postblast Residues of Ascorbic Acid Black Powder Substitutes

Because of insufficient quantities of some of the black powder substitutes listed in Table 1, two powders were selected for postblast residue analysis: Goex Pinnacle Replica Black Powder and Jim Shockey's Gold. As described earlier in the Materials and Methods section, six pipe bombs were constructed, three with Pinnacle and three with Jim Shockey's Gold. The data showed that all the postblast devices had a similar anion profile. Oxalate, along with ClO_4^- and NO_3^- from the original oxidizers, and Cl^-, ClO_3^-, NO_2^-, and HCO_3^- from the combustion products, were detected in all postblast device extracts. Of the ascorbic acid degradation products, oxalate was the most abundant and was identified in all six postblast devices. In some of the devices, oxalate's response in the mass spectrometer was too weak to make an identification, but when the electrospray cone voltage was lowered, the oxalate was clearly identified. The monohydrated diketogulonate was the smallest peak in the ascorbic acid standard's chromatogram and not surprisingly could only be detected in some of the postblast devices. Threonate is more difficult to identify in the postblast extracts because it coelutes with other peaks that appear to be additional ascorbic acid degradation products. Although threonate's characteristic peaks at m/z 75 and 135 suggest its presence, it is difficult to positively identify without a better IC separation or a different mass spectrometric method.

Figure 7*a,b* (close-up view of Fig. 7*a*) represent a typical ion chromatogram observed for the postblast extracts. The presence of m/z 75 and m/z 135 in the first peak in Fig. 7*a,b* is indicative of threonate, but a clean spectrum could not be obtained because of coeluting compounds. The third peak is the chloride ion Cl^- with m/z 35 and its isotopic peak at m/z 37 observed in the mass spectrum. The chloride ion originates from potassium chloride (KCl), the major combustion product of the oxidizer potassium perchlorate. Peaks 4 and 8 are nitrite NO_2^- (m/z 46) and nitrate NO_3^- (m/z 62 with fragment ion at m/z 46), respectively. Both nitrite and nitrate originate from the oxidizer potassium nitrate. Peak 6 in Fig. 7*a,b* contains bicarbonate (HCO_3^-) and monohydrated diketogulonate, which coelute in this method. When the relatively weak response of the extracted m/z 165 ion is compared to the conductivity detector's response, it is clear that peak 6 is largely because of the bicarbonate, with only trace levels of the monohydrated diketogulonate present. The mass spectrum of this peak, shown in Fig. 7*c*, clearly establishes the presence of both ions as m/z 61 originates from bicarbonate and the major peaks at m/z 209 and

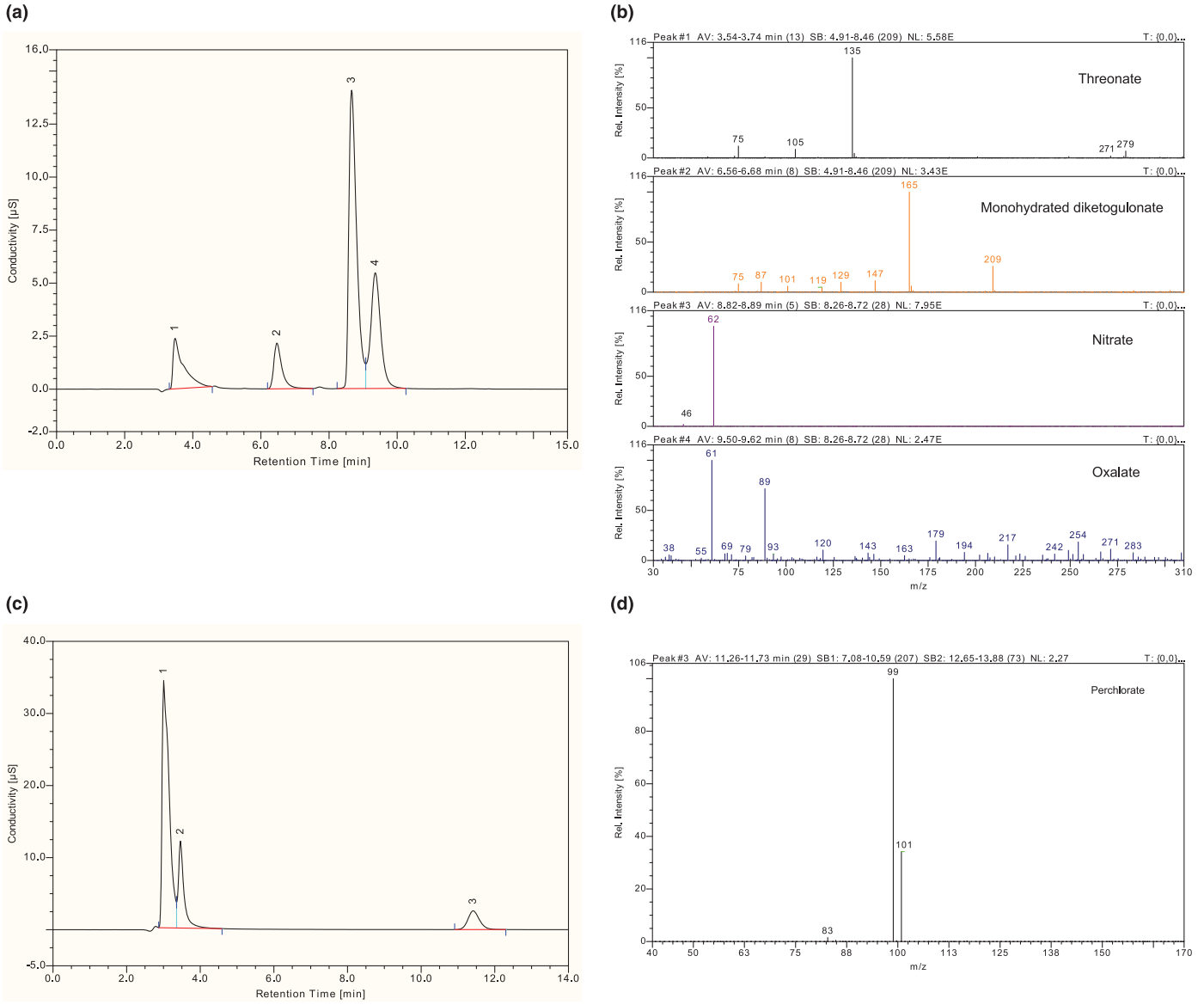

FIG. 6—*Ion chromatograms of intact Jim Shockey's Gold: (a) anion method, 1 = threonate, 2 = monohydrated diketogulonate, 3 = nitrate, 4 = oxalate; (b) mass spectra of the anions seen in Fig. 6a; (c) perchlorate method, peaks 1 and 2 = unresolved anions, 3 = perchlorate; (d) mass spectrum of perchlorate.*

m/z 165 along with minor fragments m/z 147, m/z 129, m/1 119, m/z 101, m/z 87, and m/z 75, originate from the monohydrated diketogulonate anion. Bicarbonate ions originate from potassium carbonate and/or bicarbonate, which are the other major combustion products of these ascorbic acid black powder substitutes. Peak 7 in Fig. 7*a,b* is bisulfate HSO_4^- (m/z 97 and isotopic peak at m/z 99), which is a result of the black powder pyrotechnic fuse used to initiate the device. Peak 9 contains primarily oxalate along with trace levels of chlorate ClO_3^-. The mass spectrum of this peak, seen in Fig. 7*d*, has m/z 61, 89, and 179 which originate from oxalate and m/z 83 and 85 (isotopic peak of m/z 83) which are due to the chlorate. Peaks 2 and 5 could not be identified because of high background noise in their mass spectra.

The Cl^- peak dominated the ion chromatograms of all the postblast extracts, as illustrated by Fig. 7, with one exception. The ion chromatogram for one of the Jim Shockey's Gold devices (Fig. 8) shows a large contribution from the unconsumed powder. The Cl^-, NO_2^-, and trace ClO_3^- are from postblast combustion products. The greater response for NO_3^-, oxalate, threonate, and monohydrated diketogulonate in this sample can be attributed to the presence of a larger amount of unconsumed powder on the extracted pipe fragments. This emphasizes the importance of careful microscopic examination of device fragments in explosive casework. Microscopic examination prior to extraction allows the analyst to identify the best possible fragments for analysis—for extraction, bulk techniques such as XRD, or both.

In addition to the anions previously discussed, HSO_4^-, SCN^-, and $HS_2O_3^-$ ions were identified in several samples, but they were presumably generated from the combustion of the pyrotechnic fuses used to initiate the devices. These ions, if present, were only seen in trace amounts in the postblast fragments of the two devices initiated without pyrotechnic fuse. As the ascorbic acid in these black powder substitutes is used as a replacement for sulfur, a lack of sulfur-containing anions is another good diagnostic indicator of an ascorbic acid black powder substitute, or at least a sulfur-free one such as Hodgdon Triple Seven.

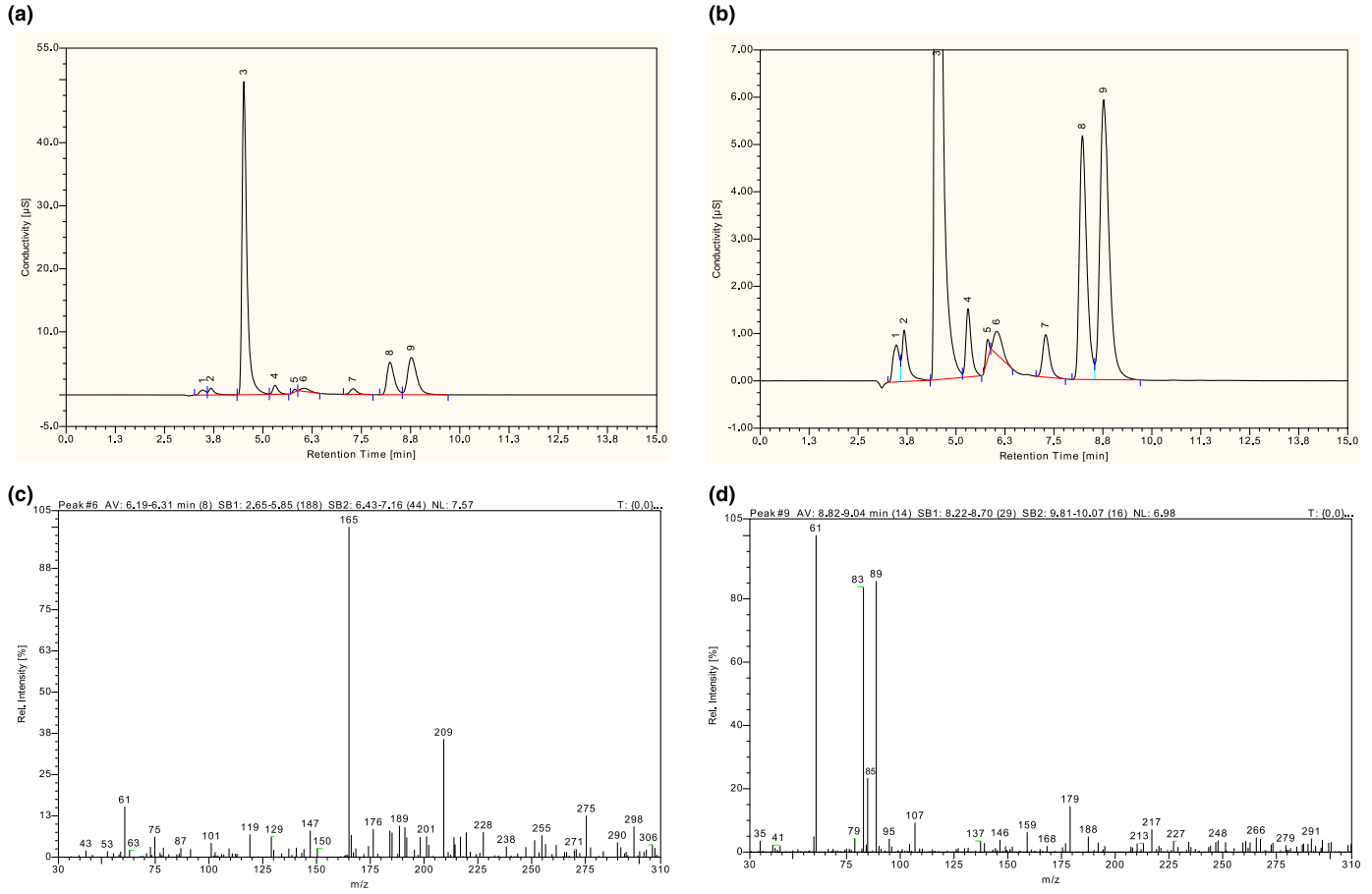

FIG. 7—*Ion chromatogram of a Pinnacle Replica Powder postblast device: (a) full scale; (b) close-up view of smaller peaks; 1 = threonate, 2 = unknown, 3 = Cl^-, 4 = NO_2^-, 5 = unknown, 6 = HCO_3^- and trace monohydrated diketogulonate, 7 = HSO_4^-, 8 = NO_3^-, 9 = oxalate and trace ClO_3^-; (c) mass spectrum of peak 6; (d) mass spectrum of peak 9.*

Chlorate Ion Formation

The ClO_3^- ion was seen in all six of the postblast device extracts, although chlorate is not one of the ingredients in Pinnacle Replica Black Powder or Jim Shockey's Gold. The assumption here is that some of the original oxidizer, $KClO_4$, is converted to chlorate. This observation is consistent with what has been seen in laboratory casework and research for other perchlorate explosive mixtures such as Hodgdon Pyrodex.

Stability of Postblast Residues on Pipe Fragments

Casework backlogs and other factors often prevent evidence from being examined immediately following an explosive incident. It is therefore important to know the stability of residues on postblast debris, especially given the fact that ascorbic acid is known to degrade more rapidly in the presence of metals (8,11).

In this study, different fragments of the same postblast pipe bomb were extracted with DI water at four different times: 2 weeks, 1, 4, and 10 months after the recovery of the postblast debris. The data showed that the extracts prepared at all four times gave similar anion profiles: the Cl^- ion dominated the chromatogram while other anions, including the ascorbic acid degradation products, were seen at much lower levels. Therefore, the postblast residue appears to be stable on the metal fragments for as long as 10 months, possibly longer.

Conclusions

This IC/MS technique is capable of identifying both the inorganic oxidizers and organic fuels for intact and postblast black powder substitutes containing ascorbic acid within a single experiment and without any additional derivatization or stabilization steps. Although the organic fuel (ascorbic acid) is not detected in its original form, its diagnostic degradation products oxalate (m/z 89), threonate (m/z 135), and monohydrated diketogulonate (m/z 209), can be identified in the intact powders. Oxalate and additional ascorbic acid degradation products can be detected in postblast residues. The full anion profile for the intact powders consisted of NO_3^-, oxalate, threonate, monohydrated diketogulonate, and ClO_4^- (for those powders with a $KClO_4$ oxidizer). The full anion profile for the two postblast powders analyzed contained a large amount Cl^-, and lower levels of ClO_4^-, ClO_3^-, NO_3^-, NO_2^-, HCO_3^-, and oxalate. The monohydrated diketogulonate and threonate could only be identified in some of the postblast samples when the electrospray cone voltage was set to 80 V. However, operating at lower cone voltages enhanced the detection of all the ascorbic acid degradation products. It is important to consider that the identification of postblast ascorbic acid black powder substitutes should be based on the complete anion profile, not merely the presence of the oxalate anion, for example. The presence of other ions, such as chloride, nitrate, perchlorate, and bicarbonate, in addition to the lack of sulfur-containing ions are all key components of the anion profile.

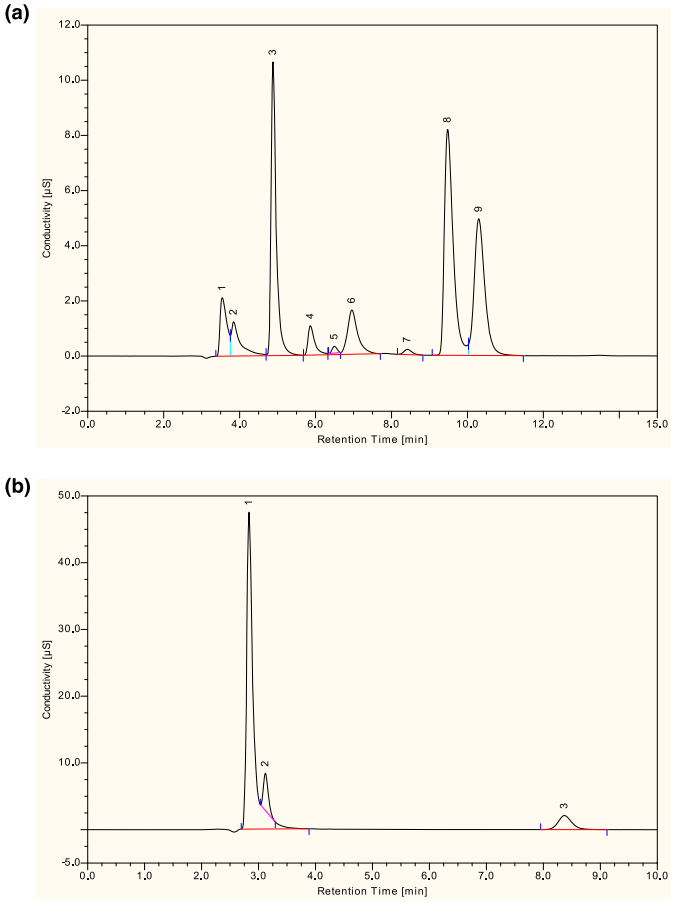

FIG. 8—*Ion chromatogram of Jim Shockey's Gold device #3: (a) anion method, 1 = threonate, 2 = unknown, 3 = Cl^-, 4 = NO_2^-, 5 = unknown, 6 = monohydrated diketogulonate and bicarbonate, 7 = HSO_4^-, 8 = NO_3^-, 9 = oxalate and trace ClO_3^-; (b) perchlorate method, peaks 1 and 2 = unresolved anions, 3 = perchlorate.*

Future Studies

The anion method that is currently employed by the ATF Forensic Science Laboratory—Washington was used as a starting point to evaluate the efficacy of analyzing ascorbic acid by IC/MS. This method was designed to detect Cl^-, NO_2^-, HSO_4^-, NO_3^-, ClO_3^-, benzoate, and $HS_2O_3^-$, listed in elution order. While this method works well for intact black powder substitutes containing ascorbic acid, it may not be the best method for analyzing postblast residues because of numerous coeluting peaks. Therefore, a revised method that focuses on separating the ascorbic acid degradation products from each other (in the case of threonate) and from other important anions (such as chlorate, which currently coelutes with oxalate) will be developed. Once the peaks coeluting with threonate are separated, these compounds may subsequently be identified. Additional modifications to the mass spectrometric method have proven to be effective and will be utilized in the future, such as operating at a lower electrospray cone voltage. In addition, the ATF laboratory is currently developing a high pressure liquid chromatography–mass spectrometry (HPLC/MS) method to identify the inorganic oxidizers and the intact organic fuel rather than the decomposition products of ascorbic acid, for this group of black powder substitutes.

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