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The Identification of the Emulsifier Component of Emulsion Explosives by Liquid Chromatography-Mass Spectrometry

ABSTRACT: The widespread availability of emulsion explosives for commercial blasting has inevitably lead to their diversion for criminal misuse. Present techniques for the characterization of emulsion explosives and their residues is generally based on the detection and identification of the oxidizer and the hydrocarbon components. Use of these components is problematic for residue identification because ammonium nitrate, waxes, and oils are relatively common in the urban environment and even their co-detection does not exclude them being sourced from materials other than explosives. The detection of the emulsifier component offers increased evidential value as certain emulsifiers used in explosive formulations are manufactured for that specific use, or have limited environmental distribution. In the current study liquid chromatography-mass spectrometry (LC-MS) was utilized for the characterization of two emulsifiers in common use; ethanolamine adducts of polyisobutylene succinic anhydride and sorbitol mono-oleate (SMO). The LC-MS technique enabled the detection of both emulsifiers in preblast samples; however, only SMO was detected in postblast residues. The analysis of the hydrocarbon component by gas chromatography-mass spectrometry was achieved in the same procedure.

KEYWORDS: forensic science, explosives, emulsion explosives, liquid chromatography-mass spectrometry, emulsifiers

Emulsions are mixtures of two immiscible liquids with one liquid phase dispersed uniformly throughout the second. Explosive emulsions are "water in oil types," wherein microscopic droplets of the concentrated oxidizer solution are surrounded by a continuous wax/oil phase, providing water resistance to the product. Emulsifiers are added to prolong the life of explosives by providing a stable interface between the oil and water phases. The emulsifier component is generally present at levels up to 5% and may also contribute to the fuel component of the explosive (1).

Compared with traditional organic explosives, there are relatively few studies on the forensic identification of emulsion explosives and their postblast residues (2–8). Previous studies rely on the analysis of the oxidizer compounds, hydrocarbons, and other components such as aluminium flakes and glass microballoons. Complete characterization of postblast residue by these methods is problematic because of the presence of the commonly used oxidizer, ammonium nitrate, and hydrocarbon fuels in the urban environment (7,9).

The characterization of emulsion explosives, including the identification of the emulsifier and hydrocarbon components using gas chromatography with flame ionization detection (GCFID) has been described (2,5). Gas chromatography-mass spectrometry (GC-MS) has been used to identify components of the emulsifier sorbitan mono-oleate (SMO) in preblast and postblast samples (6).

Liquid chromatography (LC) has proved to be applicable to the analysis of high polarity and/or high molecular weight compounds such as surfactants and emulsifiers, which are generally unsuitable for analysis by GC. LC combined with mass spectrometry (LC-MS) provides greatly increased identification power.

Emulsifiers currently used in emulsion explosives include ethanolamine adducts of polyisobutylene succinic anhydride (PIBSA) and SMO (Fig. 1). Ethanolamine PIBSA adducts are believed to be formulated principally for explosives (10) while other PIBSA amine adducts are widely used as dispersants in motor oils (10,11). Sorbitol oleates are also used as food additives, in cosmetics, in textile processing, in dry cleaning detergents and as polymer additives (12). Mixtures of PIBSA and SMO emulsifiers may be present in the same explosive (13). The aims of this study were to characterize PIBSA and SMO emulsifiers in both preblast and postblast explosive samples by LC-MS and to simultaneously identify the corresponding hydrocarbon profiles by GC-MS.

Materials and Methods

Standard Emulsifier Samples

The PIBSA adduct was supplied by Orica Explosives, Australia, while SMO was supplied by CRODA (Singapore). The emulsifiers were diluted with HPLC-grade isopropanol to 1% solutions prior to LC-MS analysis. Serial 1:10 dilutions with isopropanol were also undertaken to determine the LC-MS detection limit for both emulsifiers. Powergel Magnum 365 (Orica Melbourne,

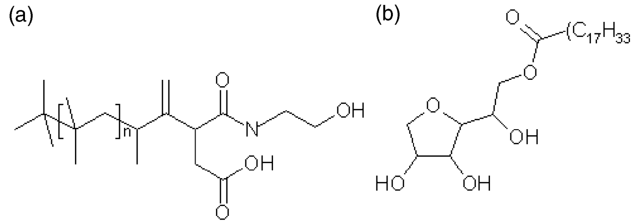

FIG. 1—*(a) Structure of polyisobutylene succinic anhydride. (b) Structure of sorbitol mono-oleate.*

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Australia), and Emulite 150 (Dyno Nobel, Sydney, Australia) cartridge explosives were purchased in Australia.

Instrumentation

The LC system comprised a Waters NovaPak (Milford, MA) C_{18} 3.9 × 150 mm column, with a Waters C_{18} Guard Column, an Agilent (Palo Alto, CA) 1100 series binary pump and autosampler. Solvent A was isopropanol containing 0.1% formic acid and solvent B was methanol.

The MS system comprised an Agilent 1100 MSD VL Ion Trap system using helium as the dampening and collision gas, while nitrogen was used as the auxiliary gas for the ion source. Direct injections were via a syringe pump at a rate of 1500 μL/h.

The GC-MS instrument included an Agilent 6890 gas chromatograph coupled to a 5973 N mass selective detector. An Agilent Ultra polydimethylsiloxane column; length 12 m, internal diameter 0.1 mm, and film thickness 0.4 μm was used. The injection volume was 1 μL.

Instrument Operating Parameters; PIBSA Analysis

The elution program for PIBSA began at 0.5 mL/min with 60% B for 1 min, changing to 40% after 3 min and 0% after 6 min. The flow rate was then changed to 0.6 mL/min until 22 min. After 22.10 min solvent B was set to 60% and the flow rate returned to 0.5 mL/min and held until 27 min. The injection volume was 1 μL.

Mass spectrometer settings included the use of atmospheric pressure chemical ionization (APCI) in positive ion mode, with a drying gas temperature of 350°C, APCI temperature of 450°C, nebulizer pressure of 60 psi, drying gas of 5 L/min, trap drive level 100% and a compound stability of 100%. The mass range scanned was *m/z* 100–2000 with a maximum accumulation time of 30 ms. MS/MS analysis of the significant structures of PIBSA included all oligomer units from the base unit of *m/z* 272 to *m/z* 1952.

Instrument Operating Parameters; SMO Analysis

The LC elution gradient for the SMO emulsifier began with 60% B for 4 min, changing to 100% B over 10 min, then back to 0% B after 15 min, and returning to equilibrium after 16 min. The flow rate was held at 0.5 mL/min, using a 1 μL injection volume.

Mass spectrometer settings included the use of the electrospray ionization (ESI) in positive ion mode with a nebulizer pressure of 40 psi, drying gas setting of 8.0 L/min, and a drying temperature of 350°C. The target mass was set at *m/z* 500 with an accumulation time of 30 ms, compound stability of 100%, and trap drive setting of 100%.

Instrument Operating Parameters; Hydrocarbon Analysis

Initial oven temperature was set at 60°C, reaching a final temperature of 310°C in 20.5 min. The mass spectrometer was operated in full scan mode (m/z 15–460).

Bulk Explosive Extracts

Portions of both Powergel Magnum 365 and Emulite 150 emulsion explosives were dissolved in both isopropanol and hexane to give standard solutions of approximately 10% w/v. The isopropanol solution was then analyzed by LC-MS for the presence of emulsifiers and the hexane solution by GC-MS for the presence of hydrocarbons Injection volumes were set at 5 μL and 1 μL, respectively.

Collection and Preparation of Postexplosion Residues

Two hundred and fifty gram cartridges (Powergel Magnum 365 and Emulite 150) were placed in cryovac plastic bags filled with yellow sand. The cartridges were initiated with a number 8 detonator. Sand from the blast seat was removed and placed in a separate cryovac bag, where it was stored pending further analysis. Two hundred grams of the soil was extracted twice with 150 mL of hexane and concentrated to approximately 20 mL. A 1 mL sub-sample was filtered through a Pasteur pipette packed with alumina, activity grade 1 (Sigma Chemicals, St. Louis, MO) and analyzed by GC-MS for hydrocarbons. The remaining extract was left to evaporate completely at room temperature before dissolving in 10 mL of isopropanol and filtration through a C18 "Sep-Pak" cartridge (Waters, Milford, MA). The filtrate was then evaporated under a stream of air before dissolving in 70 μL of isopropanol and analyzed by LC-MS for the emulsifier component.

Results and Discussion

LC-MS Analysis of the Emulsifier Standard Mixtures

PIBSA Analysis—Nonaqueous solvents were required for the elution of PIBSA because of its lack of miscibility with aqueous systems. The use of an isopropanol/methanol gradient enabled the selective elution of the full range of oligomers. The elution of the higher molecular weight oligomers was assisted by a corresponding increase of the flow rate. The APCI conditions were identified as the optimal ionization mode by experimentation with direct injection using a syringe pump.

Full-scan analysis of the PIBSA LC eluent yielded complex data because of the co-elution of multiple oligomer components. The emulsifier is a mixture of oligomeric units with molecular weights that differ by 56 amu (the mass of an isobutylene unit), and a broad, bell-shaped total ion chromatogram was observed. The oligomers detected ranged in molecular weight from 271 amu (the base unit), to 1951 amu, with the mass of the most abundant component being 945 amu.

MS/MS analysis of the mixture was used to resolve the oligomers. The major transition observed and monitored was an $[M+H]^+$-H_2O loss, where M was the molecular weight of the various oligomers. The overlaid daughter ion transition chromatogram of the mixture illustrated these transitions for all oligomers (Fig. 2). Observed splitting of the peaks in the individual daughter ion transition chromatograms was

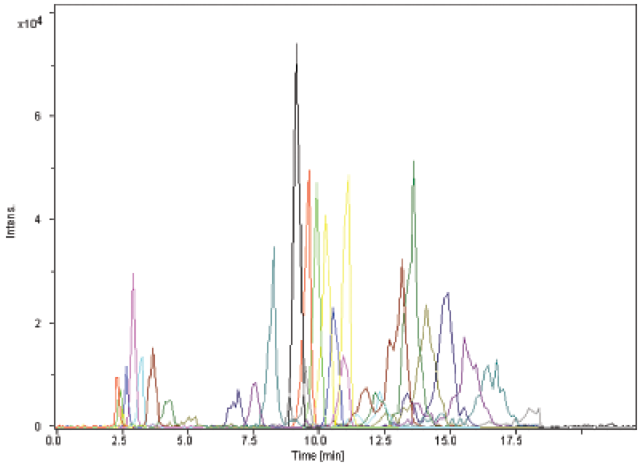

FIG. 2—*Liquid chromatography-mass spectrometry daughter ion transitions ($[M+H]^+$-H_2O) of the polyisobutylene succinic anhydride adducts, with each color representing the transition for an oligomer.*

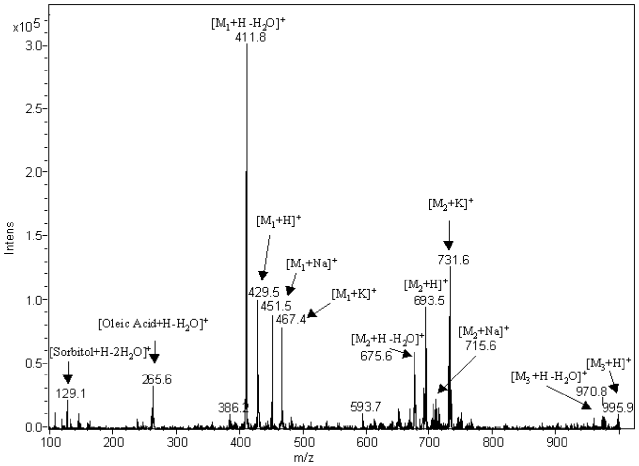

FIG. 3—*Direct injection electrospray ionization mass spectrum of the sorbitol mono-oleate emulsifier.*

attributed to the possibility of the PIBSA adduct occurring as various combinations of the ester, amide, and imide (14).

Serial dilutions of the PIBSA standard mixture were used to determine the limit of detection as approximately 30 ng/oligomer, which represented a total of 1 μg of emulsifier on column. The basis for identification of this emulsifier was the detection of 10 oligomers with a signal-to-noise ratio greater than 3:1.

SMO Analysis—ESI was identified as the optimal ionization mode for SMO by experimentation with direct injection using a syringe pump. Mass spectral information indicated the presence of the precursors, sorbitol, and oleic acid, SMO $[M_1+H]^+$, the di-oleate $[M_2+H]^+$, and the tri-oleate $[M_3+H]^+$ (Fig. 3). The $[M+Na]^+$ and the $[M+K]^+$ adduct ions were also detected for SMO and the di-oleate.

The use of an isopropanol/methanol gradient with MS/MS enabled the separation and identification of the significant components of the SMO mixture. Daughter ion chromatograms included the $[M_1+H]^+$-H_2O transitions for both the sorbitol mono-oleate (m/z 429–411) and the di-oleate (*m/z* 693–675). These ions underwent further fragmentation to produce ions related to the precursors, sorbitol (*m/z* 129), and oleic acid (*m/z* 265) (Fig. 4). The presence of a number of peaks for each transition is attributed to alternative configurations of the sorbitol mono-oleates, such as the 1, 4, the 2, 5, or the 3, 6 structures (15). Alternative configurations are also possible for the sorbitol dioleates.

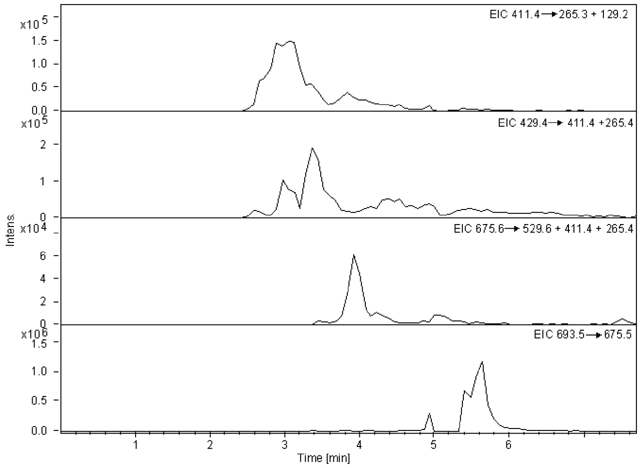

FIG. 4—*Significant liquid chromatography-mass spectrometry daughter ion transitions of the sorbitol mono-oleate components.*

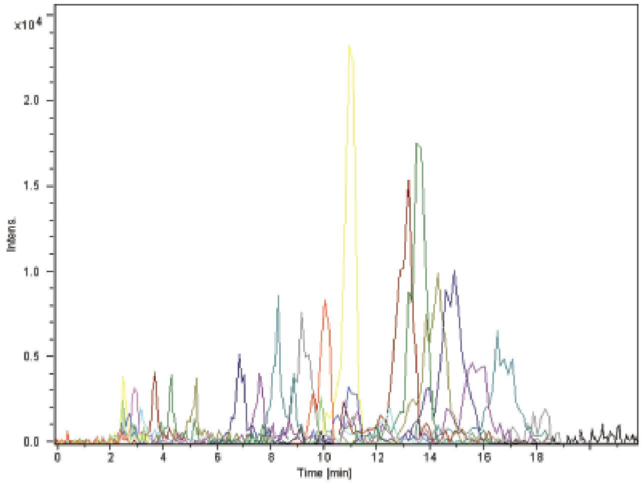

FIG. 5—*Significant liquid chromatography-mass spectrometry daughter ion transitions ($[M+H]^+$-H_2O) of PIBSA adducts from Powergel Magnum 365.*

The detection limit for SMO was approximately 2 ng per component, which represented 10 ng on column.

Bulk Explosive Analysis

Cartridge emulsion explosives were analyzed for emulsifiers by LC-MS following the procedures outlined above, yielding similar chromatograms to the standard materials (Figs. 5 and 6). Hexane extracts from the same emulsion explosives were analyzed by GC-MS. Extracted ion chromatograms (*m/z* 85) demonstrate the characteristic hydrocarbon profiles for these explosives (Fig. 7).

Postblast Residue Analysis

SMO Analysis—The MS/MS daughter ion transitions of the postblast extract of the Emulite 150 explosive indicated the presence of SMO (Fig. 8). The proportions of the various components were similar to the preblast extract.

PIBSA Analysis—In repeated experiments PIBSA was not detected in postblast samples despite the facile detection of the hydrocarbon components. The nondetection of PIBSA may be because of the relative high limit of detection of PIBSA using APCI. The limit of detection for total PIBSA was approximately 100 times higher than for total SMO. This is partially because of

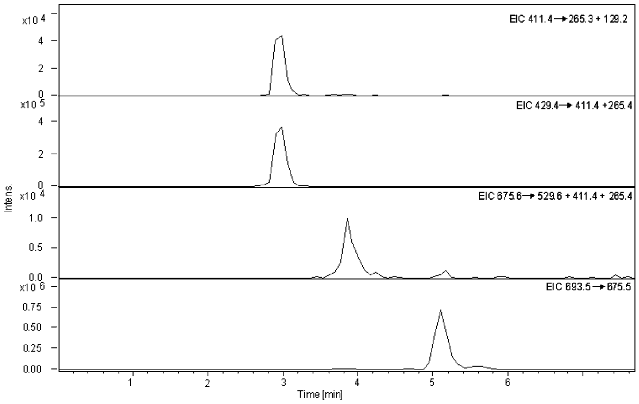

FIG. 6—*Significant liquid chromatography-mass spectrometry daughter ion transitions of the sorbitol mono-oleate components from Emulite 150.*

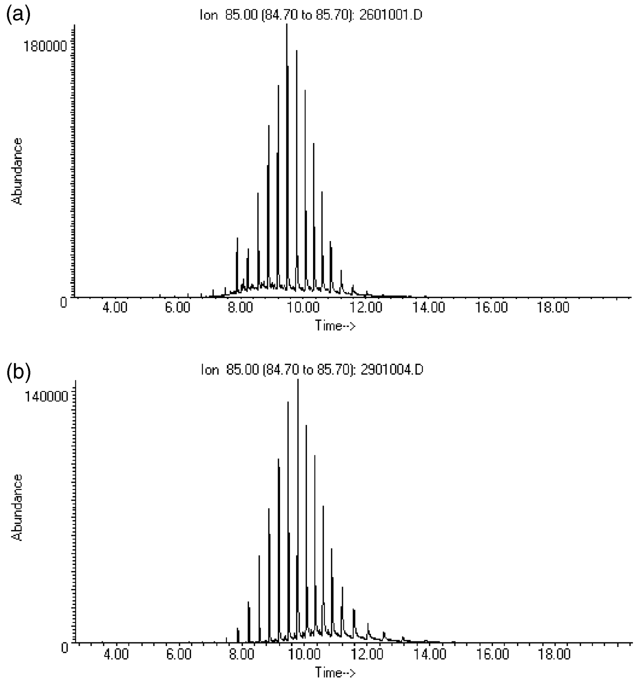

FIG. 7—*(a) Gas chromatography-mass spectrometry (GC-MS) extracted ion chromatogram (m/z 85) of the hexane extract of Powergel Magnum 365. (b) GC-MS extracted ion chromatogram (m/z 85) of the hexane extract of Emulite 150.*

the relative high number of PIBSA components per weight equivalent compared with SMO. Additionally, the emulsifier resides at the interface of the fuel and oxidizer phases and is likely to be selectively consumed during the explosion.

Hydrocarbon Analysis—The detonation of both explosives resulted in the deposition of hydrocarbons that had similar GC-MS ion chromatograms (*m/z* 85) (Figs. 9*a* and *b*). Filtering these extracts through activated alumina provided a means of removing polar contaminants (16), however, even for these relatively clean samples there was a change in the profile and a decrease of the relative heights of the *n*-alkane peaks compared with the unresolved components, illustrating the difficulty of comparing preblast and postblast samples by this technique.

Conclusion

This article describes LC-MS methods by which the commonly used emulsifiers PIBSA and SMO may be detected in emulsion explosives, thereby permitting the complete characterization of preblast material in samples such as swabs from hands, clothing, or other surfaces suspected of being in contact with explosives.

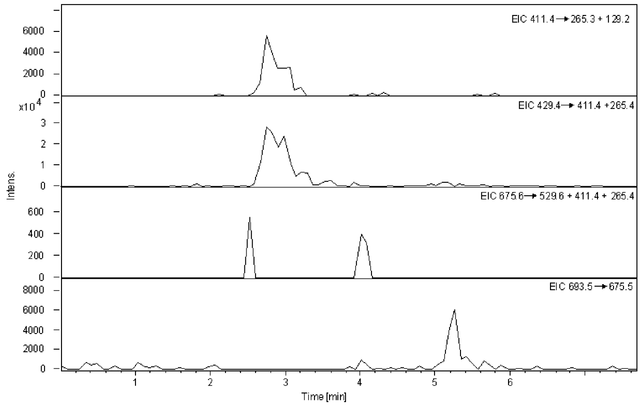

FIG. 8—*Significant liquid chromatography-mass spectrometry daughter ion transitions of the sorbitol mono-oleate components from the post-blast extract of the Emulite 150 explosive.*

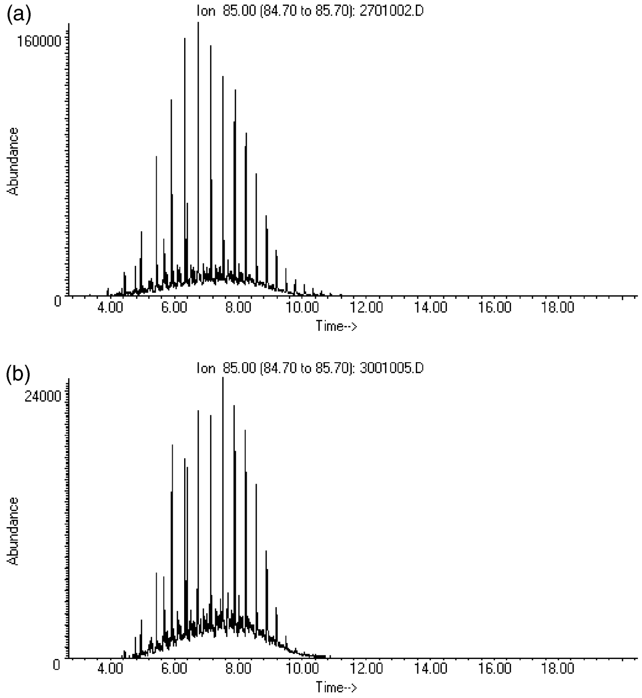

FIG. 9—*(a) Gas chromatography-mass spectrometry(GC-MS) extracted ion chromatogram (m/z 85) of the hexane extract of the postblast sample of Powergel Magnum 365. (b) GC-MS extracted ion chromatogram (m/z 85) of the hexane extract of the post-blast sample of Emulite 150.*

SMO was detected in the postblast residues of emulsion explosives, thereby providing a means of adding significant evidential value to results obtained from the suite of analyses presently available. PIBSA was not detected in postblast residues, probably because of the relatively high limit of detection for this emulsifier.

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