



Determination of emulsion explosives with Span-80 as emulsifier by gas chromatography–mass spectrometry

Fei-Fei Tian^{a,1}, Jing Yu^{b,1}, Jia-Hong Hu^a, Yong Zhang^b, Meng-Xia Xie^{a,*}, Yuan Liu^a, Xiang-Feng Wang^a, Hai-Ling Liu^a, Jie Han^a

^a Analytical & Testing Center of Beijing Normal University, Beijing 100875, China

^b Institute of Beijing Criminal Science and Technology, Beijing 100054, China

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ABSTRACT

A novel approach for identification and determination of emulsion explosives with Span-80 (sorbitol mono-oleate) as the emulsifier and their postblast residues by gas chromatography–mass spectrometry (GC–MS) has been developed. 24 kinds of emulsion explosives collected have been processed by transesterification reaction with metholic KOH solution and the emulsifier has turned into methyl esters of fatty acids. From the peak area ratios of their methyl esters, most of these emulsion explosives can be differentiated. In order to detect the postblast residues of emulsion explosives, the sorbitols in the emulsifier Span-80 obtained after transesterification reaction have been further derivatized by silylation reaction with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) as the derivatizing reagent. The derivatization conditions were optimized and the derivatives were determined by GC–MS. The results showed that the silylation derivatives of sorbitol and its isomers, combined with hydrocarbon compounds and methyl esters of fatty acids, were the characteristic components for identification of the emulsion explosives. The established approach was applied to analyze the postblast residues of emulsion explosives. It has been found that the method was sensitive and specific, especially when detecting the derivatives of sorbitol and its isomers by GC–MS in selecting ion mode. The information of the characteristic components can help probe the origin of the emulsion explosives and providing scientific evidences and clues for solving the crimes of the emulsion explosive explosion.

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1. Introduction

Identification and determination of explosives, especially their postblast residues, was an important topic in forensic science [1,2]. Determining the chemical compositions of explosives and their postblast residues can provide scientific information for differentiation of these explosives and probing their origins, and offer important clues and evidences for solving the crimes of the explosion.

Various methods have been developed for analysis of explosives and explosive residues, including ion chromatography [2–4], capillary electrophoresis (CE) [5–13], gas chromatography (GC) [14–19], GC coupled to mass spectrometry (MS) [20–25], and high-performance liquid chromatographic approaches [26,27]. Different technologies of mass spectrometry have been attempted to determine the compositions of organic explosives and detect their

residues, such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) mass spectrometry [28–31], electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry [32], isotope ratio mass spectrometry (IRMS) [33], ion mobility spectrometry (IMS) [34–36] and laser electrospray mass spectrometry [37,38]. Some new mass spectrometric devices have been designed to detect the trace explosives on various surfaces [39–41] in recent years. Fourier transform infrared spectroscopy (FT-IR) [42,43] and laser induced breakdown spectroscopy [44–47] have also been applied to measure the explosive residues.

Recent years, emulsion explosives are most widely used in China and their annual output is about 40–50% for all the explosives [48]. Emulsion explosives comprise two immiscible phases, an aqueous solution of inorganic oxidizing salt as a discontinuous phase dispersed throughout a continuous organic fuel phase, and emulsifiers are used to improve the stability of emulsion explosive composition [49]. The commonly used emulsifier is sorbitan mono-oleate (Span-80) and polyisobutylene succinimide (PIBSA) and its amount is generally within a range from 0.1 to 5.0% [50].

* Corresponding author. Tel.: +86 10 58807981; fax: +86 10 58800076.

E-mail addresses: xiemx@bnu.edu.cn, mengxia-xie@263.net (M.-X. Xie).

¹ The two authors have equal contributions to this work.

There are few publications concerning the identification of emulsion explosives [51,52]. Korosec determined the content of ammonium nitrate and sodium nitrate in explosive using thermogravimetry (TG) and differential scanning calorimetry (DSC) methods. De Tata and coauthors reported a liquid chromatography–mass spectrometry method for characterization of the emulsifiers, both Span-80 and PIBSA, while only Span-80 was detected in the postblast residues of emulsion explosives.

In this report, the identification and determination approaches for emulsion explosives with Span-80 as emulsifier and their postblast residues have been systematically investigated based on GC–MS in full scan and selected ion monitoring modes. The samples were processed with transesterification and silylation reactions, and the derivatizing conditions were optimized. The established method was sensitive, repeatable and reliable for detecting the emulsifier in the postblast residues of emulsion explosives, and the chromatographic profiles of the derivatives for sorbitol and its isomers can give rich information to probe the origin of the emulsion explosives.

2. Experimental and methods

2.1. Reagents and preparation of solutions

N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) + trimethylchlorosilane (TMCS) (BSTFA:TMCS = 99:1) were obtained from Sigma–Aldrich company (MO, USA). Methanol and hexane were HPLC grade and purchased from Dikma technology (CA, USA). The emulsifier of industrial pure Span-80 (95%) was purchased from Beijing shiji Chemical (Beijing, China). Other reagents were analytical grade and from Beijing chemical reagent factory (Beijing, China). All the reagents were used as supplied without further purification.

Emulsifier samples (Span-80) were accurately weighted (100 mg) and dissolved in a 100 ml volumetric flask with hexane. The working solutions were prepared by diluting the stock solution in hexane as required.

Methanolic KOH solution was prepared by dissolving 2.8 g KOH with 50 ml anhydrous methanol. The required concentrations can be obtained by diluting the solution with methanol.

2.2. Gas chromatography/mass spectrometry

The GC–MS analyses were performed using a Trace GC–MS spectrometer (ThermoFisher, CA, USA) equipped with a DB-5MS fused-silica capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness) which was from J & W Scientific (Folsom, CA, USA). Data was collected with an Xcalib software data process system. Complete characterization of the components was carried out in full scan mode and in selected ion monitoring mode.

The GC–MS analyses were carried out in splitless mode using high purity helium as carrier gas at a flow rate of 1 ml/min. The ion source temperature was 200 °C and the GC–MS interface was 250 °C. The injection port temperature was 250 °C; the oven was maintained at an initial temperature of 60 °C for 2 min, and then programmed at 10 °C/min to a final temperature of 290 °C where it was maintained for 10 min.

2.3. Derivatization reactions

2.3.1. Transesterification reaction for the emulsifier Span-80 and emulsion explosives

A procedure: The 10 mg emulsion explosive was extracted by hexane (10 ml) with two times, combined the extraction solutions

and filtered using a 0.45-μm nylon filter for removal of insoluble particles. The solution was then concentrated to 1.0 ml with a gentle stream of nitrogen. Add 0.1 ml 0.1 mol/ml methanolic potassium hydroxide solution to the concentrated extraction solution, and then transesterification reaction was carried out in ultrasonic bath for 15 min at room temperature.

B procedure: The 1.0 ml SP-80 hexane solution (100 μg/ml) was added with 0.1 ml 0.1 mol/ml methanolic potassium hydroxide solution, and then reacted in ultrasonic bath for 15 min at room temperature.

C procedure: The above reaction mixtures were transferred to a separatory funnel, respectively. After addition 5.0 ml hexane and 5.0 ml sodium sulfate saturated aqueous solution, the two phases were separated. The hexane layer containing the methyl esters was washed another 5.0 ml sodium sulfate saturated water solution. The hexane solution was dried with anhydrous sodium sulfate and vaporized to near dryness with a gentle stream of nitrogen. The residues were dissolved by 1.0 ml hexane and then analyzed by GC–MS instrument.

2.3.2. Acetylation and silylation reactions for the emulsifier SP-80 in explosive

Acetylation reaction: The reaction mixture obtained in B procedure was dried with nitrogen gas. Add 0.50 ml pyridine and 0.50 ml acetic anhydride to the test tube of residues, vortexed to obtain a uniform solution. Seal the tube with its plug and put the tube to a water bath with 90 °C for 40 min. The reaction mixture was dried with nitrogen gas and the residue was extracted with 2.0 ml dichloromethane, and the extraction solution was washed with saturated NaCl water solution. The dichloromethane layer was separated and dried with anhydrous sodium sulfate and then was analyzed by GC–MS.

Silylation reaction: The reaction mixtures obtained in A and B procedures were vaporized with nitrogen, individually. Add 0.50 ml pyridine and 0.20 ml BSTFA and TMCS (v/v, 99:1), vortexed and sealed the tube, and then put the tube to a water bath with 60 °C for 40 min. The reaction mixture was dried with nitrogen gas and the residue was dissolved with 1.0 ml hexane before GC–MS analysis.

2.4. Collection of samples and preparation of post blast residues

Twenty four emulsion explosives were collected from different manufacturers in various restricts of China.

Steel plates (200 cm × 100 cm, thickness 100 μm) were used to collect explosive residues from field test and were placed on the ground. The explosive device was positioned in the center of the plate. Four further plates were arranged laterally around the explosives at a distance of 1–2 m. The emulsion explosive was detonated and the residues on the steel plates were collected in polyethylene bags, which were subsequently heat-sealed to avoid contamination. Soil samples were also taken directly near the base plate both before and after the detonation [7].

The residues on each steel plate were washed with 30 ml hexane. The hexane solutions were combined and filtered using a 0.45-μm nylon filter. The solution was concentrated by rotary evaporator to about 5 ml and then transferred to a test tube. The solution in the tube was further concentrated to about 1 ml with nitrogen gas.

The soil samples (about 20 g) were extracted with 30 ml hexane twice, and the combined solutions were concentrated following above procedures.

The solutions of residues were derivatized according to above procedures of B and silylation reaction before GC–MS analysis.

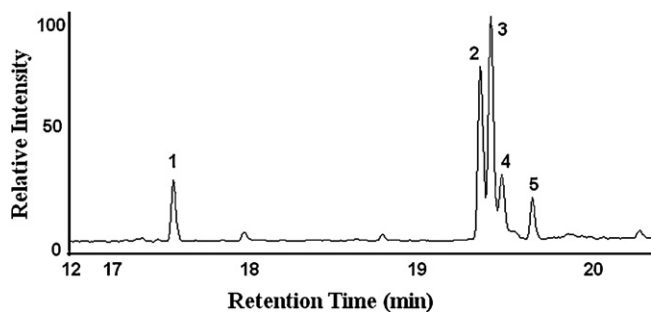


Fig. 1. The GC/MS total ion chromatogram of Span-80 after transesterification reaction, 1: methyl palmitate; 2: methyl linoleate; 3–4: methyl oleate; 5: methyl stearate.

3. Results and discussion

3.1. Differentiation of emulsion explosives with Span-80 as emulsifier

3.1.1. Separation of emulsion explosives by GC–MS

The compositions of emulsion explosives mainly include ammonium nitrate, fuels, emulsifiers, and other organic or inorganic additives [49,50], and hydrocarbons are the commonly used fuel sources.

Twenty four samples of emulsion explosives with Span-80 as emulsifier were extracted with hexane individually and the extracts were analyzed by GC–MS based on the chromatographic conditions in experimental section. The results showed that the volatile ingredients of the emulsion explosives were n-alkane with carbon number distribution ranged from C₂₁ to C₃₃ (figure not shown). The components were separated on the baseline ($R > 1.5$) and the n-alkane carbon number distribution remained constant with various samples. There was no other information about the compositions of the emulsion explosives in the chromatograms, and so it was difficult to achieve individual differentiation of these explosives due to similar chromatographic features of their hydrocarbon components.

3.1.2. Differentiation of emulsion explosives

Emulsifiers are the critical components of emulsion explosives, and the industry Span-80 is a complex mixture. It contains not only the product of a single ester and its isomer, but also other pairs of esters, multi-esters and their corresponding isomers [53]. The compositions of Span-80 from various origins would be different, and this provides a clue to differentiation of the emulsion explosives.

Span-80 is a nonionic surfactant and cannot be measured directly by GC–MS due to its non-volatile. According to the structural characteristics of Span-80, transesterification reaction was performed [54,55] in metholic KOH solution, and the fatty acids in Sp-80 molecules were dissociated and transformed into methyl esters. Fig. 1 shows the GC–MS total ion chromatogram of Span-80 after the transesterification reaction. The three main peaks in the chromatogram were determined by their MS spectra, which were methyl oleate, methyl linoleate and methyl palmitate, respectively. The boiling point of oleic acid was nearly same as that of linoleic acid, and they were difficult to be separated by rectification method, and so their mixtures were usually used to industrial synthesis of Span-80 [56,57], while palmitic acid was an impurity component of the oleic acid. The ratio of each component for these fatty acids would be different from product to product, and these differences can be utilized to differentiate the Span-80, and further to distinguishes the emulsion explosives.

Twenty-four kinds of the industrial emulsion explosives were extracted with hexane and derivatized by the transesterification

reaction as described in experimental section, and the derivatives were analyzed by GC–MS. The results showed that the relative peak area for the methyl ester of oleic acid varied from 23.7% to 97.2%, while those of linoleic acids from 73.6% to 1.2%, and the percentages of impurity, palmitic acid, were below 10% for most of the emulsion explosives. The relative standard deviations (RSD) of 5 repeats for their relative peak areas and retention time were below 2% and 1%, respectively.

Fig. 2 was the bar chart presenting the relative peak area of the methyl esters of oleic acid and linoleic acid for the 24 explosives. From the figure, it can be seen that most of the 24 explosive samples can be differentiated according to the relative intensities of the fatty acids in the derivatives of their emulsifier. In order to verify the method, 10 kinds of emulsion explosives were randomly selected from the 24 samples. The selected samples were treated with the established method and analyzed by GC–MS. The results showed that 8 samples can be differentiated from the relative peak area of the methyl esters of the fatty acids.

3.2. Derivatization of the emulsifier

The postblast residues of emulsion explosives were a complex matrix, and there have been many interferential components on the site of explosion [43]. As described above, the industrial emulsion explosives can be determined and differentiated by the presence and the ratios of the fatty acids in their emulsifier Span-80. While in the postblast residues, the fatty acids may sometimes exist in the environment, such as soil, the cotton for collecting samples, and so the fatty acids were not the characteristic components to signify the presence of emulsifier Span-80.

From the compositions of Span-80, it can be seen that sorbitols are characteristic components. Sorbitols generally exist in the fruits of plant, and they seldom occur in soils. If sorbitols have been detected from the postblast residues of explosives, it can be concluded that the explosives are emulsion explosives with Span-80 as emulsifier.

The sorbitol esters in Span-80 are non-volatile and cannot be analyzed directly by GC/MS and so derivatization reaction is needed. Direct silylation of Span-80 could improve their volatilities, and their derivatives can be separated by GC method [58]. This approach can be utilized to monitor the industrial products of Span-80, while the limits of detection were not enough to analyze the emulsifier in postblast residues of emulsion explosives.

3.2.1. Selection of derivatization reagent for sorbitols

In Span-80, sorbitols exist in various forms, 1,4:3,6-isosorbide, 1,4-sorbitan, 1,5-sorbitan and other isomers. As shown in Fig. 3, after the transesterification reaction, the Span-80 turned into the methyl esters of fatty acids and the isomers of sorbitols, which should be further derivatized before GC–MS analysis. Acetylation and silylation are usually utilized to convert alcohols into volatilizable derivatives [59–61]. In current work, the common derivatizing agents like acetic anhydride–pyridine for acetylation and *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethyl-chlorosilane (TMCS) for silylation were investigated.

The Span-80 (100 µg/ml) was derivatized with acetic anhydride and BSTFA individually after transesterification reaction as described above. The derivatives were separated by GC–MS, and their components were qualitatively determined by search from the NIST08 database which have about the mass spectra of 180,000 compounds, and then confirmed by the ion fragments of their mass spectra.

Fig. 4 shows the total ion chromatograms of the derivatives. From Fig. 4B, it can be seen that only the acetylation derivative of 1,4-sorbitan can be detected apart from the methyl esters of fatty acids, while the signal of the derivative was very weak. From the

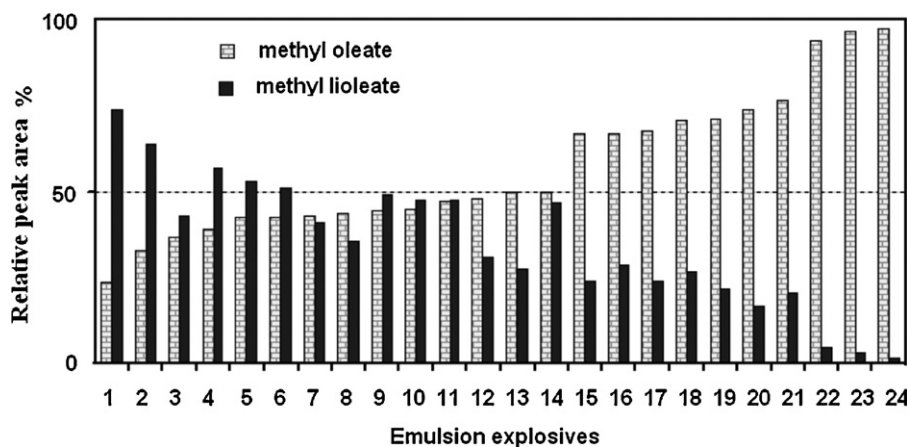


Fig. 2. The relative peak area of the methyl esters of oleic acid versus that of linoleic acid for the 24 industrial emulsion explosives. The RSD of the relative peak areas were below 2% ($n=5$).

mass spectra of the acetylation derivatives (figure was not shown), the main ion fragments of the derivatives were below m/z 100, and it indicated that acetylation reaction for the sorbitols was not suitable to monitor the postblast vestiges of the emulsion explosives. Fig. 4A shows the total ion chromatograms for the silylation derivatives of Span-80 after transesterification reaction. From the search

results and their mass spectra, the derivatives of these components were determined.

Table 1 lists the search results of the derivatives and the main ion fragments in their mass spectra apart from the fragments at m/z 73, 117, 147 of the derivating reagent and those fragments (m/z below 100). From Table 1, it can be seen that peak 1 to peak 10

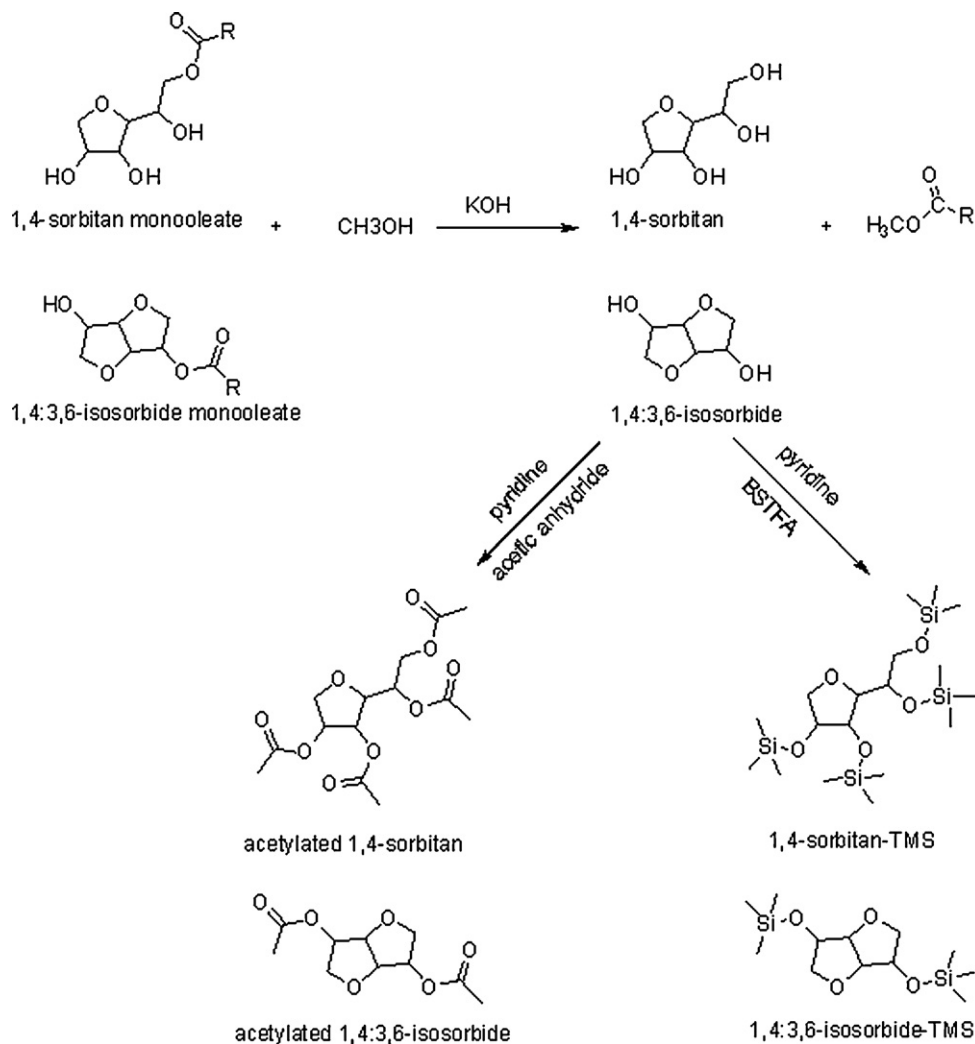


Fig. 3. The derivatization reactions of Span-80.

Table 1
Main ion fragments and search results for the silylation derivatives of Span-80.

Peak number	Molecular weight	Main ion fragments	Name of components
1	290	101(70); 143(30); 157(30); 204(25); 275(20); 290(M+,5)	1,4:3,6-Isosorbide-(TMS) ₂
2	452	103(80); 169(30); 217(100); 259(55); 272(80); 362(10)	1,4-Sorbitan-(TMS) ₄
3	452	103(40); 192(30); 205(40); 217(35); 259(40); 362(25)	Cyclized sorbitol-(TMS) ₄
4	452	103(40); 157(20); 192(30); 205(40); 217(35); 259(35); 362(30)	Cyclized sorbitol-(TMS) ₄
5	452	103(30); 192(15); 205(20); 217(55); 259(20); 362(10)	Cyclized sorbitol-(TMS) ₄
6	452	103(70); 192(80); 205(55); 217(80); 259(60); 362(20)	Cyclized sorbitol-(TMS) ₄
7	452	103(55); 157(40); 205(50); 217(50); 259(45); 362(30).	Cyclized sorbitol-(TMS) ₄
8	614	103(30); 205(40); 217(35); 307(30); 319(55)	Sorbitol-(TMS) ₆
9	614	103(60); 205(75); 217(70); 307(40); 319(65)	Sorbitol-(TMS) ₆
10	614	103(70); 205(85); 217(60); 307(35); 319(60)	Sorbitol-(TMS) ₆
11	270	129(20); 143(50); 227(25); 270(M+,30)	Methyl palmitate
12	294	109(35); 164(30); 262(25); 294(M+,15)	Methyl linoleate
13	296	109(45); 130(40); 180(30); 264(35); 296(M+,10)	Methyl oleate
14	296	109(30); 130(20); 180(20); 264(30); 296(M+,10)	Isomer of methyl oleate
15	298	74(100); 101(95); 143(30); 255(15); 298(M+,20)	Methyl stearate
16	352	110(20); 129(35); 150(20); 337(30); 352(M+,5)	Linoleic acid-TMS
17	354	129(55); 145(30); 339(55); 354(M+,10)	Oleic acid-TMS
18	356	129(45); 132(75); 145(40); 341(70); 356(M+,15)	Stearic acid-TMS

TMS: trimethylsilyl.

were the trimethylsilyl (TMS) of sorbitols and its various isomers, and other components were methyl ester or silylation derivatives of fatty acids. The intensities of these components were significant and the results illustrated that silylation of the emulsifier after transesterification reaction can give rich information of its characteristic constituents. Otherwise, the main ion fragments of the derivatives were in high mass range, which would be favor to detect the components in selected ion monitoring mode (SIM) by GC-MS.

3.2.2. Optimization of the derivatization conditions

To guarantee the repeatability and reliability of the results, the conditions of the derivatization reactions have been systematically investigated and several related factors, such as the concentration of the methanolic KOH, the amount of derivating reagent, the reaction temperature and time duration of the reaction have been optimized.

The transesterification reaction is usually carried out in alkali solution at ambient temperature, such as methanolic KOH solu-

tion. The concentrations of the methanolic KOH from 0.1 mol/l to 0.8 mol/l were tested to monitor their influence on the following silylation reaction. The time duration of the silylation derivatization reaction was 60 min and a large excess of the derivatization reagent (500 μ l) was utilized to assure the completeness of the derivatization reaction. The results showed that the total peak area of the sorbitol trimethylsilyl derivatives (peak 1 to peak 10 in Fig. 4A) remained constant when the concentration of methanolic KOH was below 0.2 mol/l, while the peak area gradually decreased with further increasing the alkali concentration. In higher alkali concentration, Span-80 would be saponified in some extents, which may hinder the silylation reaction of the sorbitols. Therefore, the concentration of the methanolic KOH was fixed at 0.1 mol/l.

The reaction was conducted under 25, 40, 60, 90 °C, individually, to investigate the influence of temperature on the derivatization reaction. The results indicated that the peak area of the sorbitol derivatives reached constant when the temperature was above 40 °C. In order to increase the reaction rate, the derivatizing reaction was performed at 60 °C.

The amount of BSTFA and the duration of reaction time on the peak area of sorbitols-TMS derivatives were also optimized. 100 μ l, 200 μ l, 300 μ l, 400 μ l and 500 μ l derivative reagents were tested, respectively. The results showed that the derivatization reaction can be conducted completely when the amount of derivative reagent was above 200 μ l. The duration of reaction ranged from 20 min to 80 min was tried and the results showed that the peak area of sorbitol derivatives can be reached constant with above optimized conditions when the reaction time was 40 min.

In conclusion, the optimum conditions for the derivatization reaction were as follow: the concentration of the methanolic KOH for transesterification reaction of Span-80 was 0.1 mol/l; the silylation reaction was conducted under 60 °C for 40 min with 200 μ l derivatization reagent of BSTFA. The sorbitol derivatives were stable, and the relative standard deviations (RSD) of their peak area and retention time within 10 h were below 3% and 1%, respectively.

Based on the derivatizing procedures established above, five different concentrations of Span-80 (10, 25, 50, 100, 200 μ g/ml) were derivatized and analyzed by GC-MS in full scan mode. The linearity between the peak areas of the sorbitol derivatives and the corresponding concentrations of Span-80 was satisfactory, and the linear regression equation was $y = (0.0108 \pm 0.0006)x - (0.0608 \pm 0.0042)$ ($n = 5$, $R = 0.995$) in the concentration range from 10 to 200 μ g/ml. The limits of detection for Span-80 were 1.0 μ g/ml according to the signal-to-noise ratio of 3. The results indicated that the established approach has high sensitivity and with satisfactory repeatability,

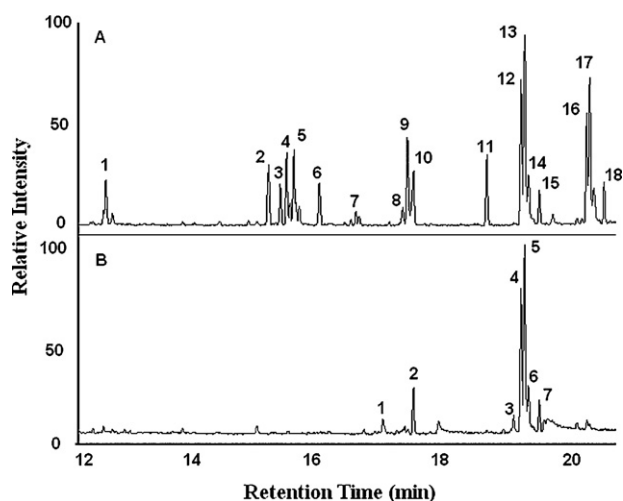


Fig. 4. (A) The GC-MS total ion chromatogram Span-80 (100 μ g/ml) after transesterification and silylation reactions. Peak: (1) 1,4:3,6-isosorbide-TMS; (2) 1,4-sorbitan-TMS; (3–7) isomers of cyclized sorbitol-TMS; (8–10) uncyclized sorbitol-TMS; (11) palmitic acid-TMS; (12) methyl linoleate; (13–14) methyl oleate; (15) methyl stearate; (16) linoleic acid-TMS; (17) oleic acid-TMS; (18) stearic acid-TMS. (B) The GC-MS total ion chromatogram of Span-80 (100 μ g/ml) after transesterification and acetylation reactions. Peak: (1) acetylated 1,4-sorbitan; (2) methyl palmitate; (3) acetylated sorbitol; (4) methyl linoleate; (5–6) methyl oleate; (7) methyl stearate.

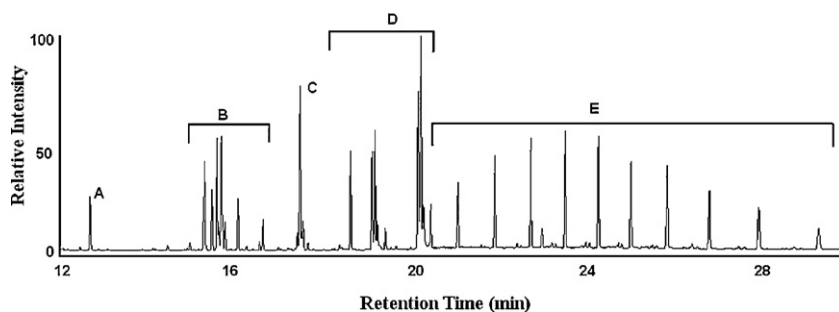


Fig. 5. The GC–MS total ion chromatogram of the emulsion explosive after derivatization reactions, the explosives was 10 mg, component A: 1,4:3,6-isosorbide–TMS; B: isomers of cyclized sorbitol–TMS; C: uncyclized sorbitol–TMS; D: fatty acid methyl ester; E: n-alkane with carbon number distribution ranged from C₂₁ to C₃₃.

and can be utilized to detect the postblast residues of the emulsion explosives.

3.3. Analysis of emulsion explosives

The analytical procedure established above was used to analyze the characteristic components of emulsion explosives, and Fig. 5 shows the full scan GC–MS chromatogram for emulsion explosives after transesterification and silylation reactions. In Fig. 5, the components A, B and C were the silyl derivatives of sorbitol and its isomers; components D were the derivatives of fatty acids, and components E were hydrocarbon compounds. These characteristic components can determine the emulsion explosives.

In order to improve the sensitivity for detecting sorbitols and its isomers, selected ion monitoring mode (SIM) was employed in GC–MS analysis. The ions selected for trimethylsilyl (TMS) derivative of 1,4:3,6-isosorbide were 290(M⁺), 275(M-15⁺, loss of a –CH₃) and 157 (M-133⁺, loss of –O–Si(CH₃)₃ and fragment –CH₂–CH₂–O–). The mass spectra of components B were similar, and so the ions selected in this time window were same, 362(M-90⁺, loss of (CH₃)₃SiO– and H), 259 (M-193⁺, loss of (CH₃)₃SiO–, (CH₃)₃SiO–CH₂– and H) ion and 217 (M-235⁺, loss of (CH₃)₃SiO–, (CH₃)₃SiO–CH₂– and fragment –CH–CH₂–O–); For components C, the selected ions were 319((M-295⁺, loss of 2(CH₃)₃SiOCH₂– and (CH₃)₃SiO–), 217 (M-397⁺, loss of 3(CH₃)₃SiO– and (CH₃)₃SiOCH₂– and fragment –CH–CH₂–), 205 (ion fragment (CH₃)₃SiO–CH+–CH₂–SiO(CH₃)₃).

Fig. 6 shows the GC–MS chromatogram of sorbitol derivatives in SIM mode. It can be seen from Fig. 6 that the signals of the derivatives were significant and the limits of detection for the emulsion explosive were below 1.0 μg/ml. The method established can be

utilized to monitor sorbitols in the postblast residues of emulsion explosives.

The hydrocarbon compounds in Fig. 5 were normal alkyl paraffins and their chromatogram can be further processed by extracted ion chromatogram (*m/z* 85) [52] (see Fig. 7). The extracted ion chromatogram of the hydrocarbon compounds can clearly display characteristic profiles of these components.

3.4. Postblast residue analysis of emulsion explosives

The described method was applied to identification for the postblast residues of emulsion explosive (the same emulsion explosive as investigated in Section 3.3). The residues were collected and pre-treated with transesterification and silylation reactions, and then analyzed by GC–MS in full scan mode. Fig. 8 shows the total ion chromatogram for the postblast residues of the emulsion explosive. It can be seen from the profile of Fig. 8 that the characteristic components of the emulsion explosive (components A–E) remained in the residues.

The chromatogram profiles of sorbitol components would become clearer when the postblast residues of the emulsion explosives were monitored by GC–MS in SIM mode (see Fig. 9). As shown in Fig. 9, the sorbitol components for postblast of emulsion explosive remained comparing with that for the original emulsion explosive, while profiles of the components have been changed. Table 2 lists the relative peak area (%) of the sorbitol–TMS derivatives in Fig. 6 for the emulsion explosive and those in Fig. 9 for the explosive residues. It can be seen that percentages of component 2 and 4 significantly increased and component 5–8 obviously reduced, while the variations of component 1 and 3 were unapparent. Blank measurements (the soil in the site of explosion) were

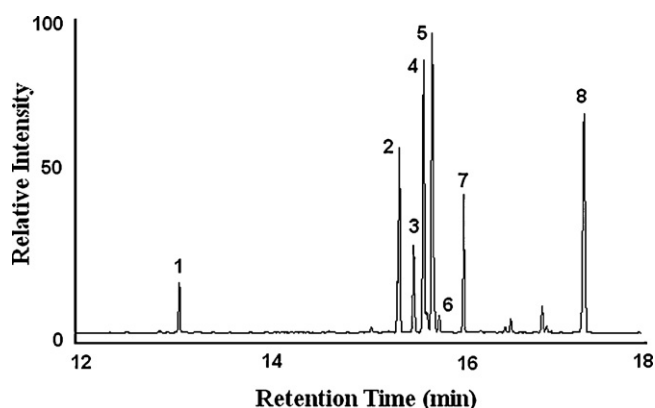


Fig. 6. The GC–MS selected ion chromatogram of the emulsion explosive after derivatization reaction, the explosive was 10 mg, peak: (1) 1,4:3,6-isosorbide–TMS; (2–7) 1,4-sorbitol–TMS and its isomers; (8) sorbitol–TMS.

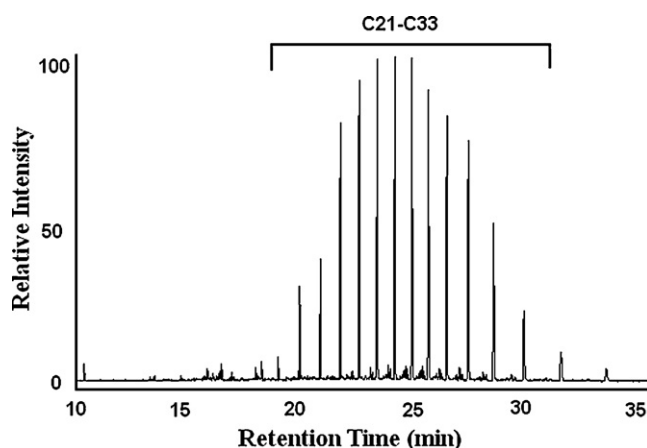


Fig. 7. Extracted ion chromatogram (*m/z* 85) of the hydrocarbon compounds in the emulsion explosive.

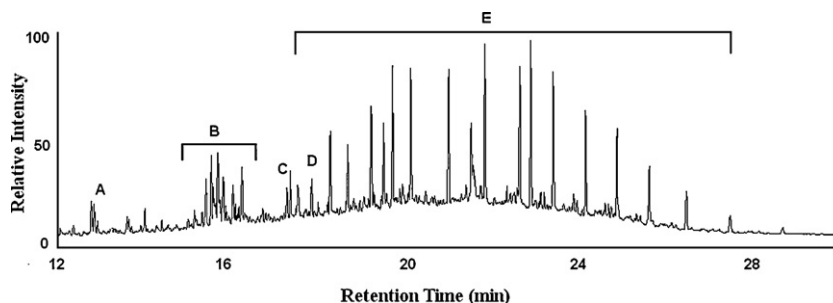


Fig. 8. The total ion GC/MS chromatogram in full scan mode for the postblast emulsion explosive residues after derivatization reactions. Components A: 1,4:3,6-isosorbide-TMS; B: isomers of cyclized sorbitol-TMS; C: uncyclized sorbitol-TMS; D: fatty acid methyl ester; E: n-alkane with carbon number distribution ranged from C₁₆ to C₃₁. The emulsion explosive for explosion was 300 g.

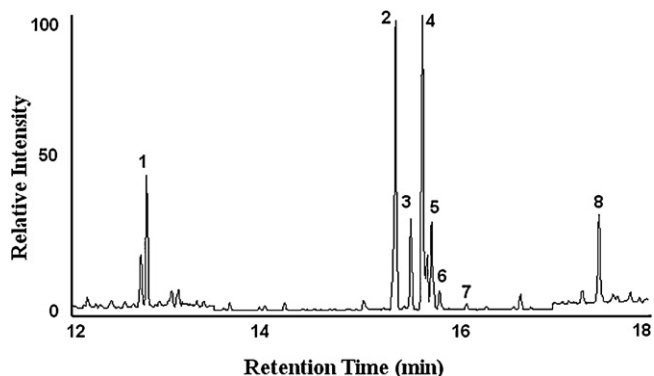


Fig. 9. The selected ion GC/MS chromatogram of the postblast explosive residues. Peak (1) 1,4:3,6-isosorbide-TMS; (2–7) 1,4-sorbitan-TMS and its isomers; (8) sorbitol-TMS.

Table 2

The relative peak area (%) of the sorbitol-TMS derivatives for the preblast and postblast of the emulsion explosive.

Peak	1	2	3	4	5	6	7	8
Preblast	8.9	14.8	10.3	18.5	18	4.6	8.6	16.3
Postblast	12.8	28.9	9.17	29.3	8.4	1.8	0.8	8.8

RSD < 3% (n = 5).

performed in the same method and the results indicated that there was no interference for identification of the sorbitol and its isomers. The information obtained could be potentially used for determining the origin and kinds of the emulsion explosives.

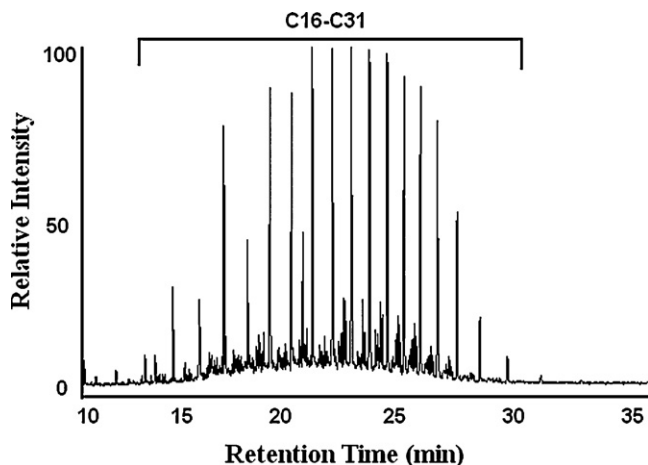


Fig. 10. Extracted ion chromatogram (m/z 85) of the hydrocarbon compounds for the postblast emulsion explosive residues.

Fig. 10 shows the extracted ion chromatogram (m/z 85) of the hydrocarbon components in the postblast residues of the emulsion explosive. It can be seen that the carbon number distribution of hydrocarbon components was between C₁₅ and C₃₁, which have some differences with that of preblast emulsion explosive (see **Fig. 7**, which was between C₂₁ and C₃₃). It showed that the hydrocarbon components underwent degradation during the process of explosion. The chromatogram profiles of the hydrocarbon components appeared as Gauss distribution. The experimental results also indicated that the carbon number distribution of hydrocarbon components changed into C₁₄ and C₂₅ when the emulsion explosive was increased to 600 g. The phenomena were similar with those [52] previously reported.

4. Summary and conclusions

Twenty four kinds of emulsion explosives with Span-80 as emulsifier were collected and analyzed by GC-MS in full scan and SIM modes. The emulsifier Span-80 was not volatile, and the GC-MS chromatograms for emulsion explosives can only give the information of hydrocarbon components. After transesterification reaction in the methanolic KOH solution, Span-80 can be turned into sorbitols and methyl esters of fatty acids, which can be analyzed by GC-MS. The presence of emulsifier derivatives in emulsion explosives served as a useful marker to distinguish from other inorganic or organic explosives. From the ratios of different fatty acid methyl esters, most of the emulsion explosives collected can be individually identified.

In order to establish an approach for determining the postblast residues of emulsion explosives, the emulsifier Span-80 was derivatized with BSTFA after transesterification reaction, and the derivatizing conditions were optimized. The derivatives were separated by GC-MS method, and the components of sorbitols were measured from their mass spectra. The established method was applied for analysis the postblast residues of emulsion explosives, and several classes of characteristic components, including sorbitol and its isomers, fatty acid methyl esters, and hydrocarbon compounds, have been detected. From the chromatographic profiles of these components, the kinds of emulsion explosives could be possibly inferred.

The results showed that the established approach could be utilized to detect the postblast residues of emulsion explosives in complex matrix and provide scientific evidences and clues for solving the crimes of the emulsion explosive explosion.

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