

TECHNICAL NOTE

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Identification of Sugars in Explosive Residues by Gas Chromatography-Mass Spectrometry

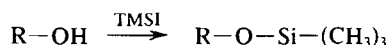
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ABSTRACT: Chlorate/sugar mixtures are commonly used in improvised explosive devices. Sugars in the burnt chlorate/sugar residues are derivatized using trimethylsilylimidazole (TMSI) in pyridine. The resulting sugar-TMS derivatives are analyzed by gas chromatography-mass spectrometry. The presence of chlorates or byproducts of the chlorate/sugar reaction do not interfere in this process.

KEYWORDS: criminalistics, chemical analysis, sugars, explosives, gas chromatography-mass spectrometry, derivatization

It is a common occurrence for homemade explosive devices to contain sugar as the fuel constituent mixed with an oxidizer such as sodium or potassium chlorate. Sugar in unexploded mixtures can be isolated and readily identified instrumentally by X-ray diffraction (XRD) or infrared spectroscopy (IR) [1]. When working with burnt residues from postblast recovered fragments of the device, however, XRD and IR may not be adequate for identifying the sugar as a result of the presence of large amounts of sodium or potassium chloride and other reaction byproducts. Chemical spot tests using naphthol [2] or ammoniacal silver nitrate [3] can be more sensitive than XRD or IR but lack specificity.

Gas chromatography-mass spectrometry (GC-MS) is an obvious choice when one needs a sensitive instrumental technique for identifying organic compounds in mixtures. A well-established technique for performing gas chromatographic analysis of products containing sugar is to convert the sugar to its trimethylsilyl (TMS) derivative [4]. The general derivatization reaction is:



Our work investigates the feasibility of derivatizing sugars in postblast residue and identifying the resulting sugar-TMS compounds by their mass spectra.

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Materials

All analyses were performed on a Hewlett Packard 5890 GC with a 5970 mass selective detector (MSD) and Chem Station Data System. The column was a HP-1 cross-linked methyl silicone fused silica capillary (Hewlett-Packard), 25 m long, 0.2-mm inside diameter, and 0.5- μm film thickness. The GC was operated in the split injection mode at a ratio of 75:1. Helium carrier gas was used at a flow rate of 0.5 mL/min. The oven was programmed from 140 to 280°C at 8°C/min after a 3-min initial delay.

Tri-Sil® Z derivatizing reagent (trimethylsilylimidazole in pyridine) was obtained from Pierce Chemical Company, Rockford, Illinois. All sugars and potassium chlorate were reagent grade.

Infrared spectra were obtained on a Nicolet 5DX Fourier transform infrared (FTIR) spectrometer, obtaining ten spectra per sample at 4-cm⁻¹ resolution.

Method

Unburned Sugar

Approximately 30 mg of pure sugar was ground in a mortar. For those samples that contained potassium chlorate, approximately 30 mg of it was ground separately and mixed with the ground sugar. The sugar or chlorate/sugar mixture was placed in a glass vial, then 0.5 mL of Tri-Sil Z was added. The mixture was heated in a 70°C oven for 10 to 30 min, shaken periodically to ensure complete dissolution of the sugar. One microlitre of the solution was injected into the GC.

Explosive Residue

Approximately 10 g of a 50:50 potassium chlorate/sucrose mixture was placed in a 10-cm-long copper pipe which was sealed by end caps and duct tape. Standard green hobby fuse was used to detonate the device. After detonation, the main body of the copper pipe was recovered. The burnt residue was extracted from the pipe with distilled water. The water extract was filtered using Whatman 41 filter paper and was evaporated on a hot plate until only a small volume of solution remained, then was transferred to a 95°C oven overnight where it evaporated to dryness. This residue, approximately 100 mg, was then ground and dried for an additional hour to ensure removal of all moisture. The Tri-Sil Z reagent was then added to half the residue and the reaction allowed to proceed as above.

Complete drying of the residue is necessary because water reacts with the silylating reagent, inhibiting the derivatization of the sugar [5]. The final drying should be done in an oven rather than allowing the extract to become dry on the hot plate to prevent a reaction from occurring with consequent loss of sensitivity between any unconsumed sugar and the oxidizer.

Results

Six common sugars were derivatized and analyzed by GC-MS. The total ion chromatogram (TIC) of a mixture of fructose, dextrose, mannitol, sucrose, and maltose derivatives is presented in Fig. 1. Reducing sugars will give multiple peaks as a result of tautomeric forms [4]. Mass spectral data for each sugar derivative are presented in Figs. 2 and 3. Lactose-TMS derivative has the same retention time as sucrose-TMS derivative under these chromatographic conditions. However, they are easily differentiated by their mass spectra (Fig. 3).

The TIC and mass spectral data obtained from the derivatization of unburned potassium chlorate/sucrose and potassium chlorate/dextrose mixtures were identical to that of the

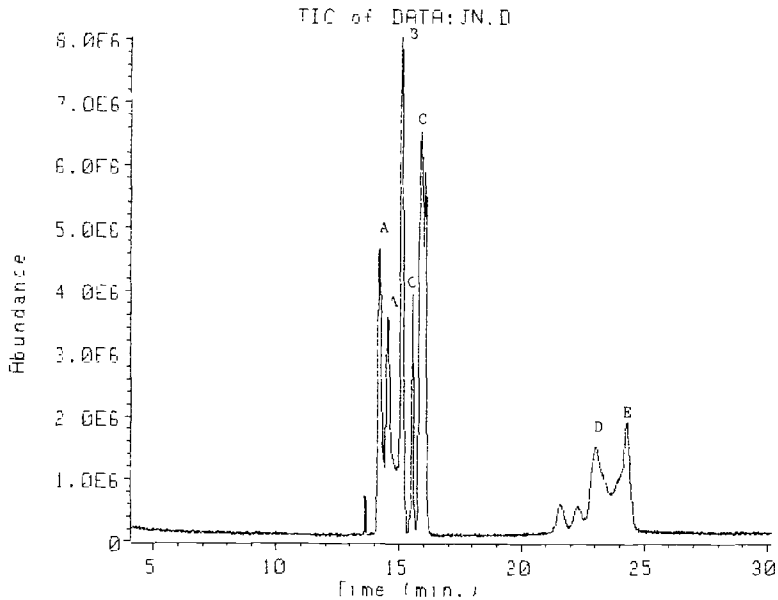


FIG. 1—Total ion chromatogram of the trimethylsilyl (TMS) derivatives of a mixture of (a) fructose, (b) dextrose, (c) mannitol, (d) sucrose, and (e) maltose.

pure sugars, indicating that the presence of potassium chlorate has no effect on the derivatization reaction.

Additional samples using decreasing amounts of sucrose mixed with an equal amount of potassium chlorate were prepared and analyzed. As little as 100 μg of sucrose is detectable by this method.

A portion of the extracted residue from the copper pipe was analyzed by FTIR (Fig. 4). The presence of sucrose in the extract is not apparent from the IR spectra. However, the presence of sucrose can be confirmed by GC-MS analysis of the derivatized residue (Fig. 5).

The presence of water will decrease the sensitivity of the technique, therefore, it is crucial that the extract be thoroughly dried in a 95°C oven before adding the silylating reagent. Sulfuric acid was also found to inhibit the derivatization reaction. This will cause problems when analyzing chlorate/sugar bombs that had been initiated by a delay mechanism using sulfuric acid.

Conclusion

Gas chromatography-mass spectrometry is a specific and sensitive technique for identifying sugars in the postblast debris of improvised chlorate/sugar explosive devices. Derivatization of the sugar before GC-MS analysis is a simple process, not subject to interference from the presence of chlorate or products of the chlorate/sugar reaction. For maximum sensitivity, care must be taken that the water extract of the postblast debris be slowly but thoroughly dried before proceeding with the derivatization procedure.

Acknowledgments

The potassium chlorate/sucrose pipe bomb was prepared and detonated by Mr. James Crippen of the Missouri State Highway Patrol. Miss Pauling's participation in this project was part of an internship program with the University of Strathclyde, Glasgow, Scotland.

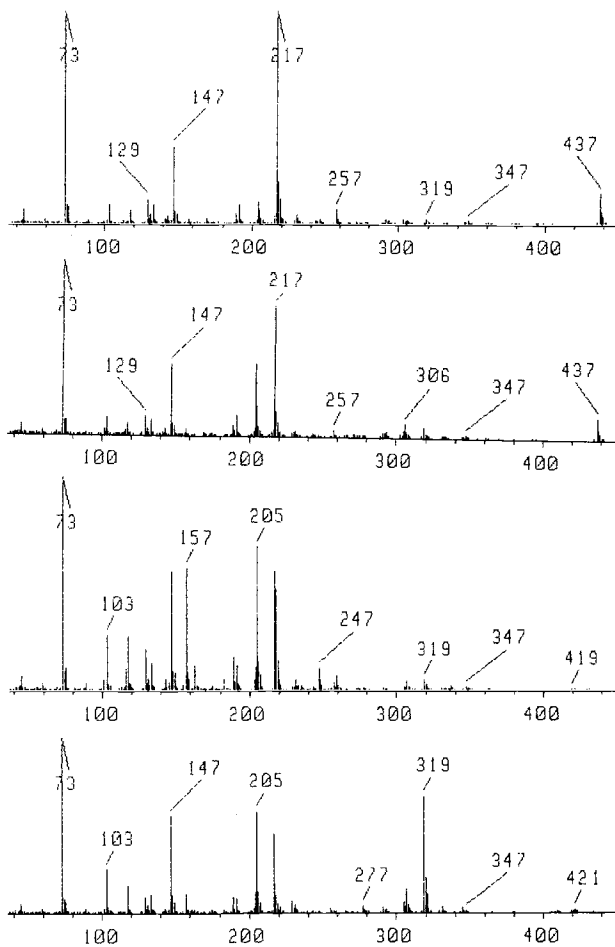


FIG. 2—Mass spectra of trimethylsilyl (TMS) derivatives of (a) fructose (first peak), (b) fructose (second peak), (c) mannitol (first peak), and (d) mannitol (second peak).

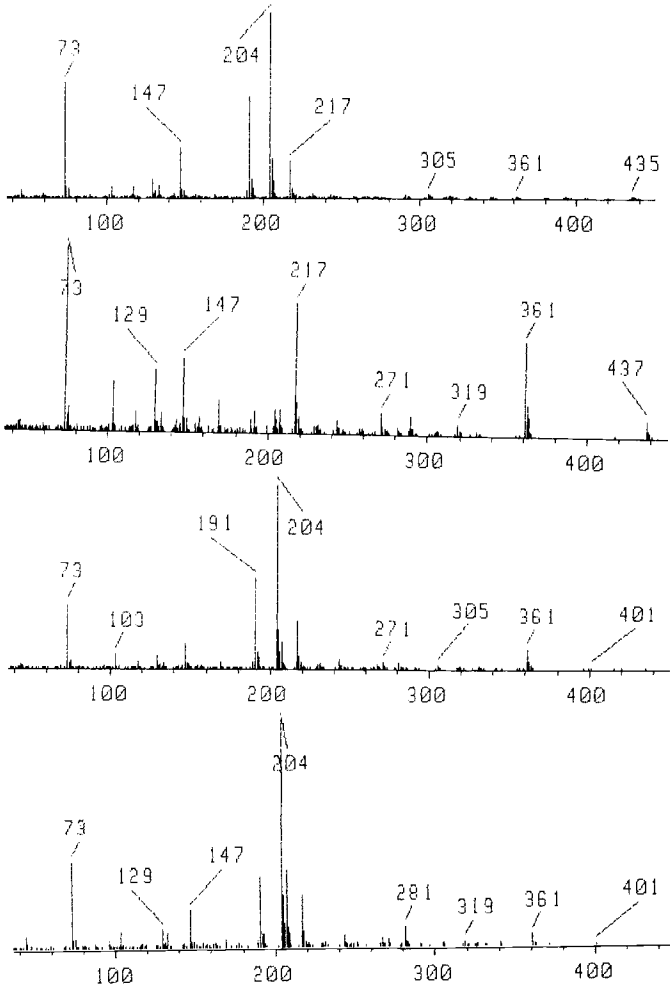


FIG. 3—Mass spectra of trimethylsilyl (TMS) derivatives of (a) dextrose, (b) sucrose, (c) maltose, and (d) lactose.

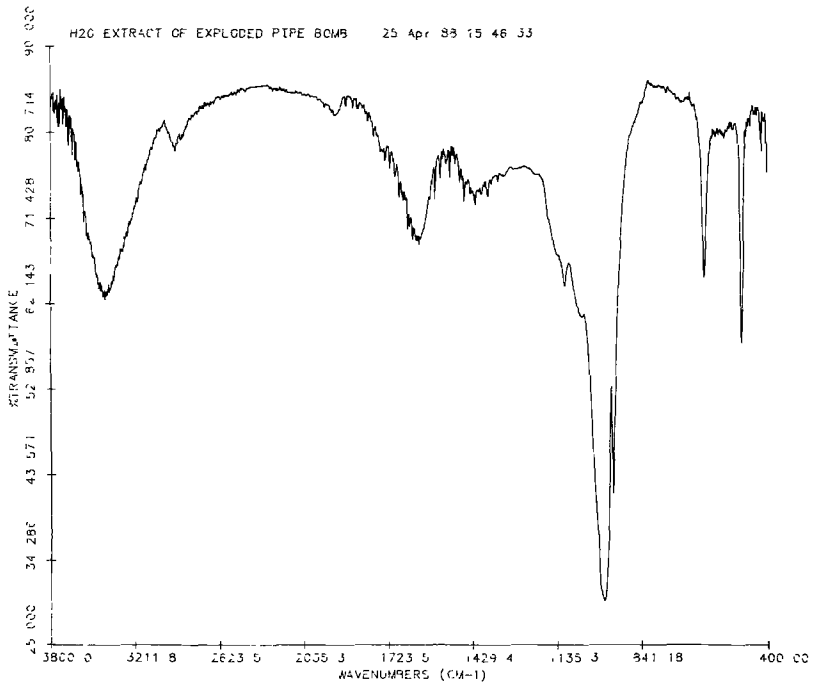
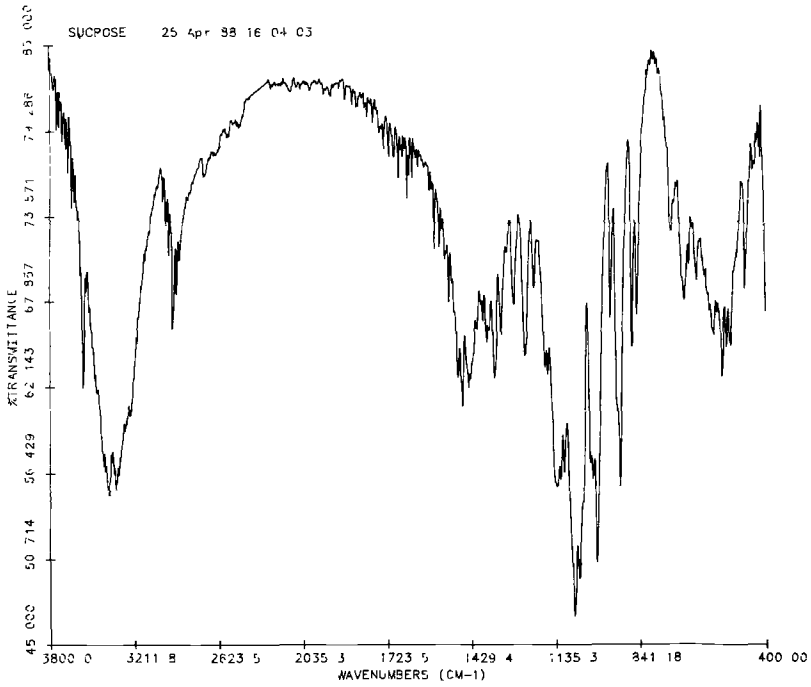


FIG. 4—Infrared spectra of sucrose (top) and dried water extract from exploded potassium chlorate/sugar bomb (bottom).

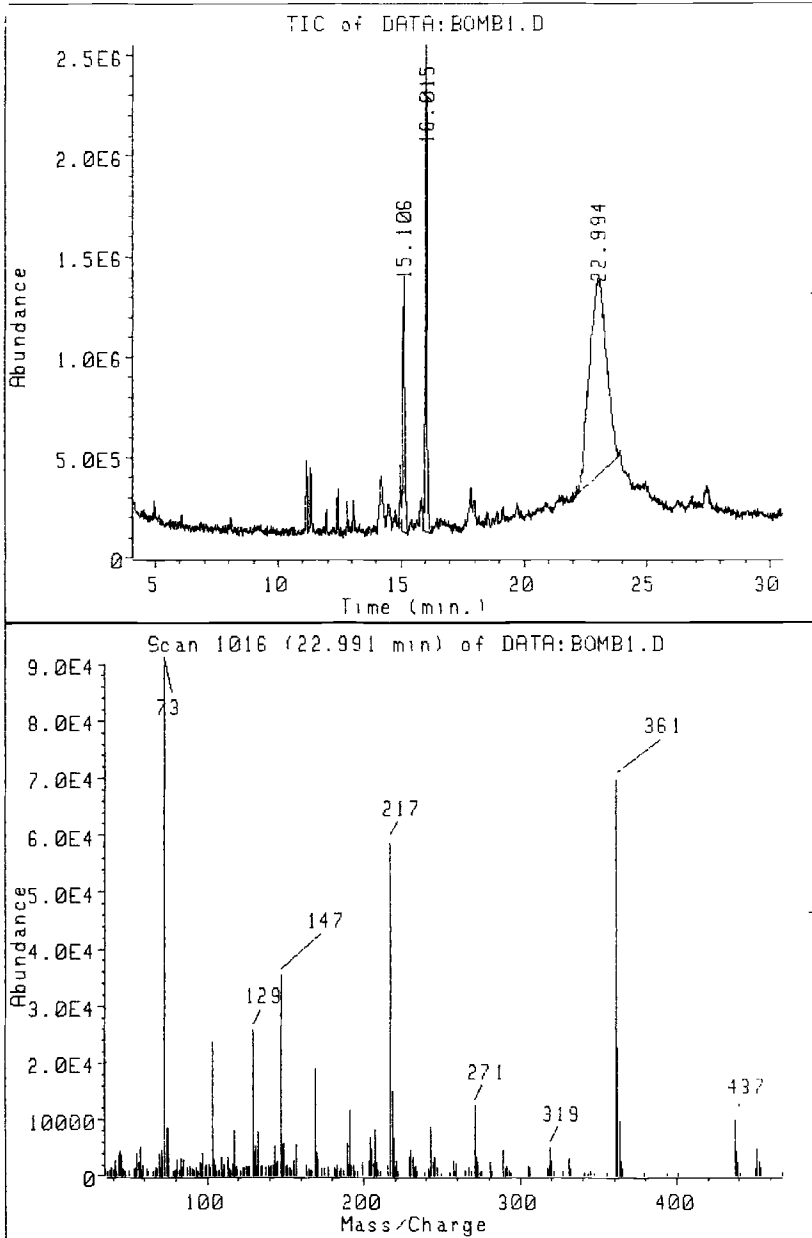


FIG. 5—Total ion chromatogram (top) and mass spectra of sucrose-TMS peak (bottom) from derivatized extract of a potassium chlorate/sucrose pipe bomb.

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