

## TECHNICAL NOTE

Michelle R. Reardon,<sup>1</sup> M.S.F.S. and Edward C. Bender,<sup>1</sup> B.S.

# Differentiation of Composition C-4 Based on the Analysis of the Process Oil\*

**ABSTRACT:** United States military Composition C-4 explosive contains 91% cyclotrimethylene trinitramine (RDX), 5.3% dioctyl sebacate or adipate (DOS or DOA), 2.1% polyisobutylene (PIB), and 1.6% oil. The original military specification required low viscosity engine oil, but this has since been changed to a specially manufactured mineral oil, also called "process oil." Differentiation of military and commercial Composition C-4 may be possible by analyzing the oil. In this study, samples of Composition C-4 were taken from various lots of U.S. military M112 demolition blocks from two commercially manufactured brands sold in the U.S. The oil and plasticizer were extracted with pentane, and the plasticizer was removed using silica solid phase extraction cartridges. The oil was then analyzed by high-temperature gas chromatography/mass spectrometry (HTGC/MS). Results indicated that HTGC/MS is an excellent discriminating technique for oil comparisons; however, differentiation of Composition C-4 is limited by manufacturer production and distribution practices.

**KEYWORDS:** forensic science, explosives analysis, Composition C-4, process oil, mineral oil, high-temperature gas chromatography/mass spectrometry

Holston Army Ammunition Plant (AAP) near Kingsport, Tennessee, has manufactured explosives, including Composition C-4, for the U.S. military since the early 1940's. In 1999, BAE SYSTEMS Ordnance Systems, Inc., became the contractor in charge of production at Holston (1). According to the military specification, Composition C-4 contains 91%  $\pm$  1.0% cyclotrimethylene trinitramine (RDX) and 9.0%  $\pm$  1.0% polyisobutylene (PIB) binder (2). The contents of this binder were approximately 2.1% PIB, 5.3% of either di-(2-ethylhexyl)-sebacate (dioctyl sebacate, DOS) or di-(2-ethylhexyl)-adipate (dioctyl adipate, DOA), and 1.6% lubricating oil, grade 10 (3,4). With the development of multi-viscosity motor oils, the original type of engine oil was no longer appropriate; thus Holston AAP found a supplier that could provide a specially manufactured oil to suit their needs (R. Keto, personal communication, 2001). The current oil used in Composition C-4 production is a low-viscosity mineral oil, also referred to as the process oil.

The analysis of Composition C-4 has generally involved solvent extraction and separation of the various components for analysis by infrared spectroscopy (5–7). Previous researchers have suggested examining the process oil by gas chromatography and have used this technique in the analysis of the oils in Semtex, a Czechoslovakian plastic explosive (5,8,9). The process oil can easily be removed by an initial extraction in a nonpolar solvent such as pentane. The solvent will remove the oil, plasticizer and lower oligomers of PIB with the explosive remaining insoluble. The plasticizer can be removed by passing the pentane through a silica solid phase ex-

traction cartridge of appropriate capacity. The extract is then analyzed by high-temperature gas chromatography/mass spectrometry (HTGC/MS), which is the ideal technique for the separation of high molecular weight hydrocarbons, such as waxes, greases, and oils, at temperatures above 350°C (10–21).

Part of a forensic chemist's role is to associate or differentiate evidence recovered from different sources. More importantly, significance must be assigned to this association or elimination. This study uses HTGC/MS to analyze the process oils in military lots and commercial sources of Composition C-4 in order to determine the comparative value of the oil analysis.

## Methods

### Samples

Samples of Composition C-4 were taken from U.S. military M112 demolition blocks and two commercial sources. There were 12 different known military lots, produced between 1968 and 2001, and three unknown military lots. Two blocks of one military lot were received from different locations, and four blocks of one military lot were received from the same location. See Table 1 for the sample list.

### Extraction

Approximately 0.5 g samples of Composition C-4 were extracted in a vial with 6 mL of pentane (Burdick and Jackson, Muskegon, MI). The vial was shaken to mix the sample and solvent, and then the precipitate was allowed to settle. The pentane extract was passed through a Sep-Pak<sup>®</sup> cartridge (Waters Corporation, Milford, MA) packed with 1 g of silica. Another 6 mL of pentane were passed through the cartridge to remove the remaining oil. Both aliquots

<sup>1</sup> Bureau of Alcohol, Tobacco, Firearms and Explosives, Forensic Science Laboratory, Ammendale, MD.

\* Presented at the 8th International Symposium on the Analysis and Detection of Explosives, June 7, 2004, Ottawa, Canada.

Received 31 July 2004; and in revised form 6 Nov. 2004; accepted 6 Nov. 2004; published 6 April 2005.

TABLE 1—Sample list.

Lot	Brand	Year	Type
A-1	...	1997*	Military
A-2	...	1997*	Military
B	...	1975	Military
C	...	1994	Military
D	...	1968	Military
E-1	...	1989†	Military
E-2	...	1989†	Military
E-3	...	1989†	Military
E-4	...	1989†	Military
F	...	1978	Military
G	...	2001	Military
H	...	2001	Military
I	...	1997	Military
J	...	1997	Military
K	...	2001	Military
L	...	1970	Military
Unknown	...	...	Military
Unknown	...	...	Military
Unknown	...	...	Military
...	X	...	Commercial
...	Y	1999	Commercial

\* Two blocks with the same lot number received from separate locations.

† Four blocks with the same lot number received from the same location.

were collected into a glass vial that was sealed with a Teflon®-lined cap. A sample from this vial was transferred to a 2 mL autosampler vial for HTGC/MS analysis.

#### Instrumentation

Extracts were analyzed in triplicate on a Perkin Elmer (Perkin Elmer, Inc., Wellesley, MA) Clarus 500 Gas Chromatograph/Mass Spectrometer equipped with a Programmable Temperature Vapor-

izer (PTV). An aluminum clad 25 m × 0.22 mm ID HT5 capillary column (SGE, Inc., Austin, TX) with a 0.1 μm film was used. The carrier gas was hydrogen at a constant flow of 1 mL/min. Injections of 2 μL were made with a 30:1 split ratio. The PTV was heated ballistically to 480°C, held for 2 min, reduced to 400°C, and held for 3 min. The initial oven temperature was 100°C with a 1 min hold, and then increased at a rate of 15°C/min to 370°C, with a final 5 min hold at 370°C. The transfer line and source were maintained at 300°C. The quadrupole MS was operated in the electron impact mode with an ionization energy of 70 eV. A full scan from m/z 40 to 450 was performed at 0.15 sec/scan.

## Results and Discussion

### Intra-lot Comparisons

The initial phase of the study involved determining the homogeneity of the process oil within one military M112 demolition block of Composition C-4. The block representing Lot A-1 was sampled in nine locations, including the surfaces and core of both ends and middle of the block. Figure 1 is a comparison of the three core samples and Fig. 2 shows representative total ion chromatograms of three of the six surface samples. The hydrocarbon pattern extends from approximately C<sub>20</sub> to C<sub>36</sub> and is similar to a low viscosity mineral oil. The chromatograms in Figs. 1 and 2 demonstrate the homogeneity of the process oil throughout the block.

The repeating groups of four peaks in the chromatograms represent the lower molecular weight oligomers of PIB that were extracted from the C-4 and not removed by the solid phase extraction cartridge. Since the concentration of these PIB oligomers varies, the interpretation of the data could be affected. Examination of a selected ion chromatogram at m/z 97 will determine which differences are attributable to PIB.

To determine homogeneity within a lot, two blocks of Lot A (A-1 and A-2) and four blocks of Lot E (E-1, E-2, E-3, and E-4)

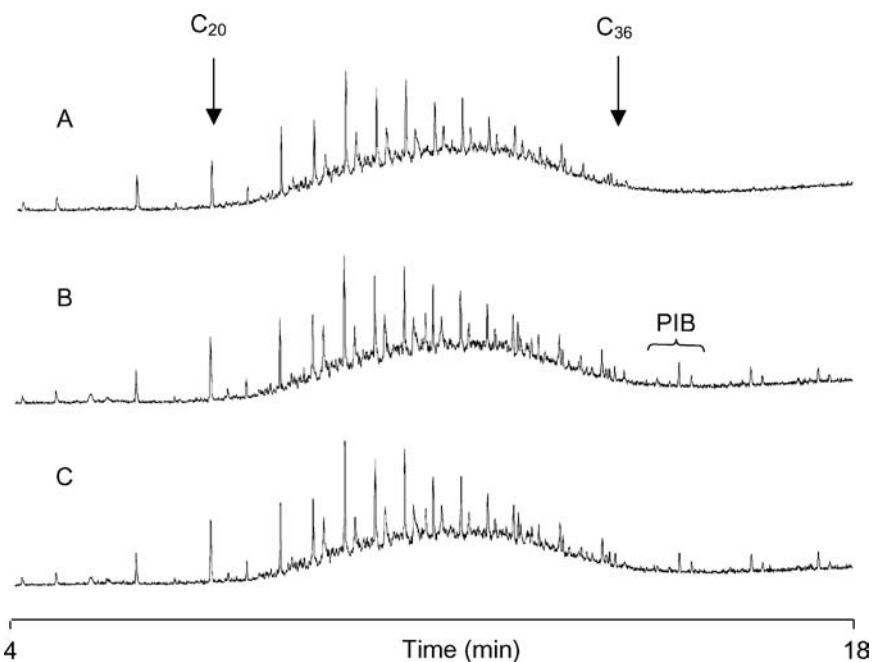


FIG. 1—Total ion chromatograms of core samples from Lot A-1. A, B, and C are from the bottom left, top right, and center of the block, respectively. The hydrocarbon patterns span from approximately C<sub>20</sub> to C<sub>36</sub>. Repeating groups of four peaks are from polyisobutylene (PIB) that could not be separated from the process oil.

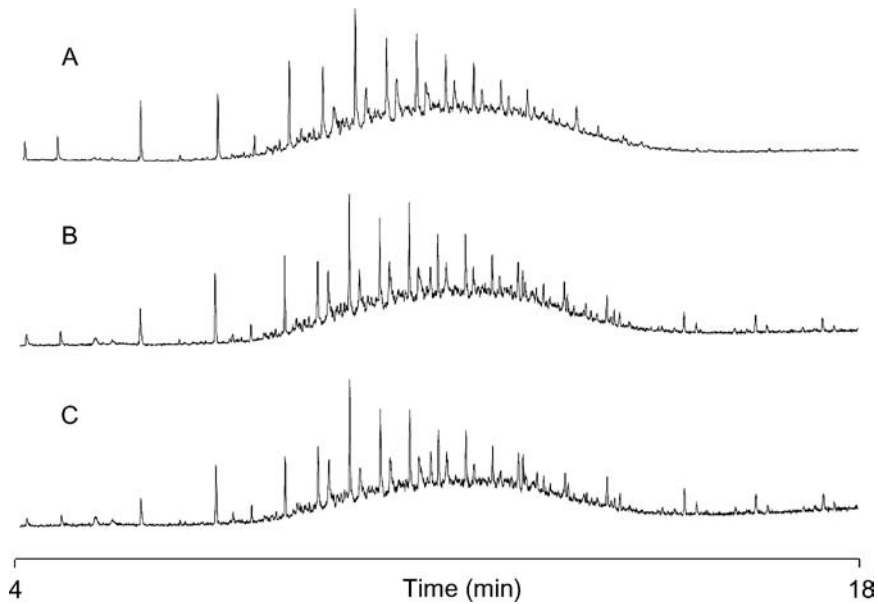


FIG. 2—Total ion chromatograms of three of the six surface samples from Lot A-1. A, B, and C are from the bottom left, top right, and center of the block.

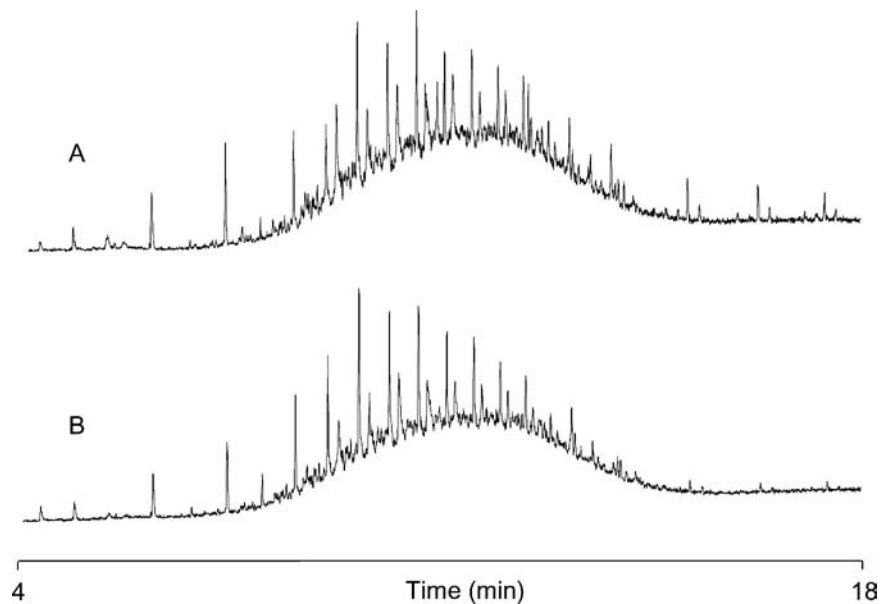


FIG. 3—Total ion chromatograms of a 1997 military lot, A-1 (B) and Lot A-2 (A).

were also examined. Samples of Lots A-1 and A-2 were received from separate locations, but samples of Lots E-1 through E-4 were received from the same location. Figures 3 and 4 are comparisons of Lots A-1 and A-2 and Lots E-1 through E-4, respectively. The chromatograms of Lot A and Lot E show that the oils are consistent within each lot but different between lots, based on the shape and width of the unresolved envelope and the number, separation, and height of peaks on top of the envelope.

#### Inter-lot Comparisons

The final phase of the study examined the process oils in samples taken from various military lots and from two commercial sources. The military samples represented lots produced between 1968 and 2001, as well as three unknown lots. Commercial Brand

Y was manufactured in 1999. Brand X did not have a lot number, although it was obtained in 2002. Representative chromatograms of the known military lots from 2001 are displayed in Fig. 5 and of the commercial brands in Fig. 6. The hydrocarbon patterns for the military lots and for the commercial brands are all markedly different by HTGC/MS. (Brand X had significant compositional differences and was distinguished from Brand Y and the military lots prior to the process oil analysis.)

The chromatograms of the unknown military lots were compared to each other and to the known military lots. Two of the three unknown lots were consistent but were different from the third. Lot D (1968) was similar to two of the unknown samples, although there was a small, unresolved envelope of heavier hydrocarbons present in the unknowns. The third unknown was similar to Lot F (1978), but the width of the unresolved envelope in the unknown was smaller (Fig. 7).

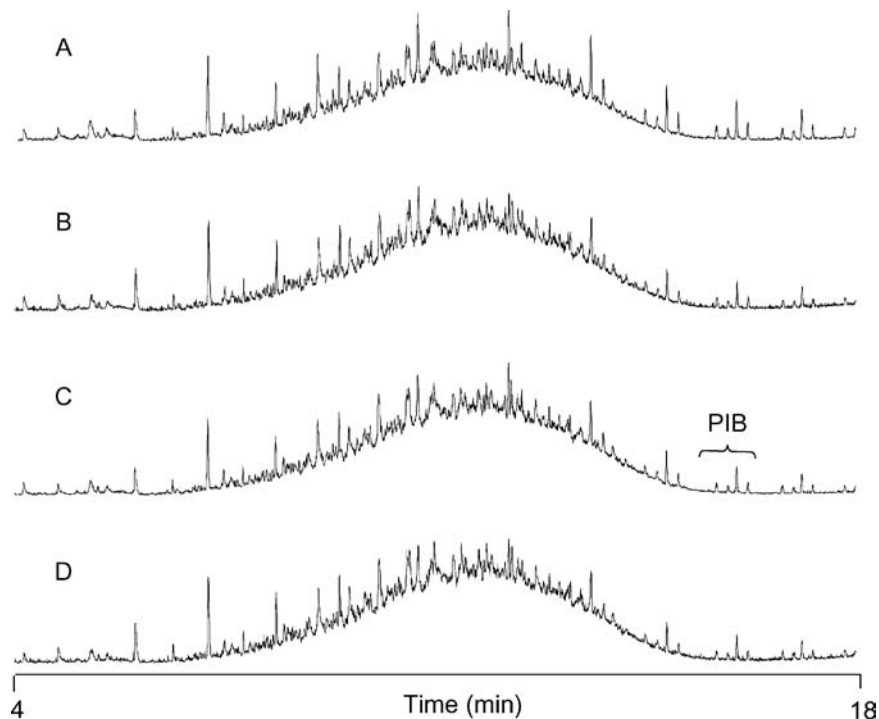


FIG. 4—Total ion chromatograms of a 1989 military lot, E-1 (D), E-2 (C), E-3 (B), and E-4 (A). The concentration of the lower molecular weight oligomers of PIB varied, as shown in these four chromatograms.

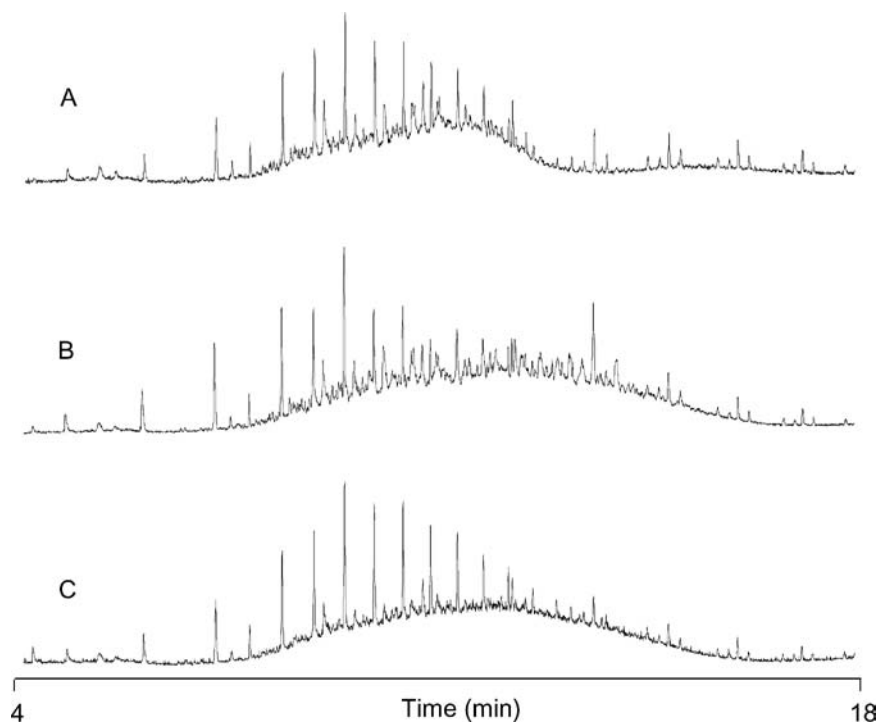


FIG. 5—Total ion chromatograms of three different military lots from 2001, Lot G (A), Lot H (B), and Lot K (C). Differences are noted in the shape and width of the unresolved envelopes.

The process oil suppliers and the Composition C-4 manufacturers are primarily interested in the physical properties of the oil, such as viscosity, which is a measure of a liquid's ability to flow (A. Wilson and G. Dockery, personal communication, 2004). These oils would most likely be indistinguishable based on a measurement of their viscosity alone. HTGC/MS is more discriminating, since it

is able to separate, define the distribution, and identify the individual constituents of the oil.

The analysis and differentiation of military lots and commercial sources based on the process oils initially appeared promising. The process oils differed between the lots of Composition C-4 and between the commercial sources. Closer examination of the data,

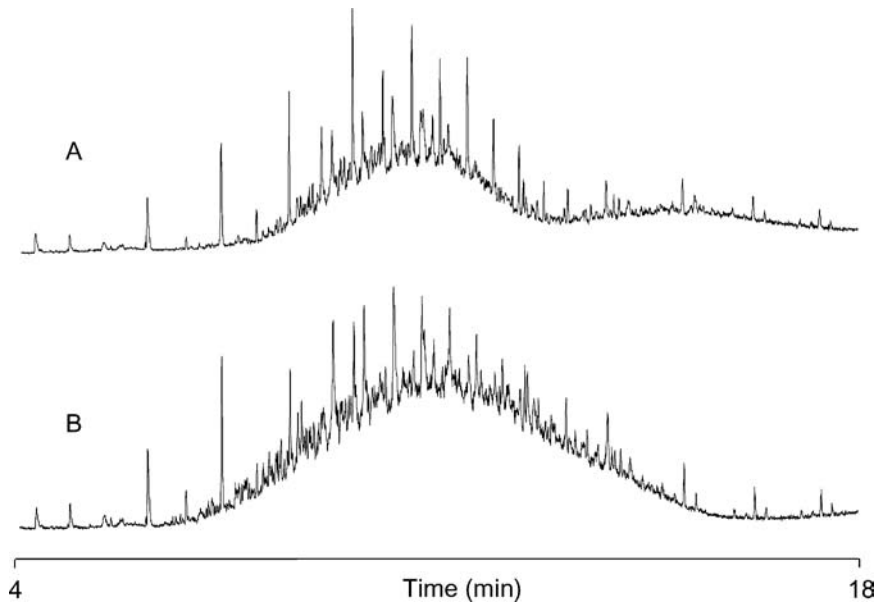


FIG. 6—Total ion chromatograms of the process oils from two commercial sources, Brand X (A) and Brand Y (B).

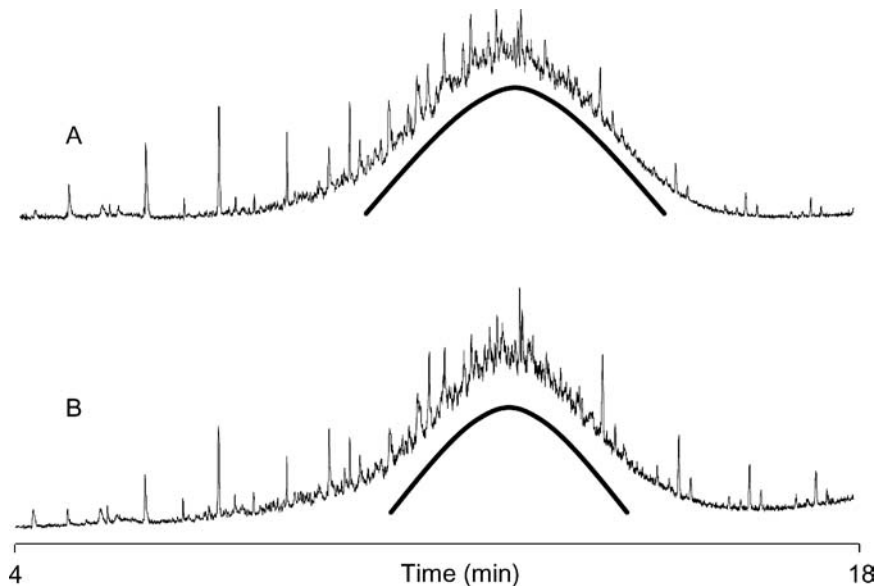


FIG. 7—Total ion chromatograms comparing a 1978 military Lot F (A) and an unknown military lot (B). The width and curvature of the unresolved envelope in the unknown differ from Lot F.

however, revealed two different lots that were indistinct. There were three lots from 1997, Lots A, I, and J. Lot A was distinguishable from Lots I and J, but Lots I and J were indistinguishable from one another (Fig. 8). Further investigation into the production and packaging process at Holston AAP led to the following information about lot number assignments (G. Dockery and B. Fly, personal communication, 2004): Military Composition C-4 is produced in 3000 kg (6600 lb) batches, and multiple batches are combined to make one lot, which is given one lot number. Because of the amount of process oil required to generate one batch, more than one lot of process oil may be used for several batches. Thus, one lot of Composition C-4 from Holston AAP will contain multiple batches and possibly more than one lot of process oil.

The Composition C-4 is shipped to the assembly and packaging facility at Milan AAP in Milan, Tennessee, in 27 kg (60 lb) boxes.

Milan then uses approximately 1000 boxes to produce one packaged lot of M112 demolition blocks, which is assigned a lot number independent of the one applied at Holston. If, for example, Holston produces a lot that contains 56,700 kg (125,000 lb) of Composition C-4, this amount would generate approximately two packaged lots from Milan. The final lot number is assigned by Milan AAP in accordance with a military standard (MIL-STD-1168) and would be in the following format: MA-00A000-000, where MA represents the packaging facility (Milan), 00 is the year (2000), A corresponds to the month (January), 000 is the lot interfix (number assigned by the manufacturer), and 000 is the lot sequence (22,23). For example, MA-04A001-001 represents the first lot produced by Milan AAP with interfix 001 that started production in January 2004.

Given the production, packaging, and lot numbering system, it would be difficult to differentiate military lots of Composition C-4

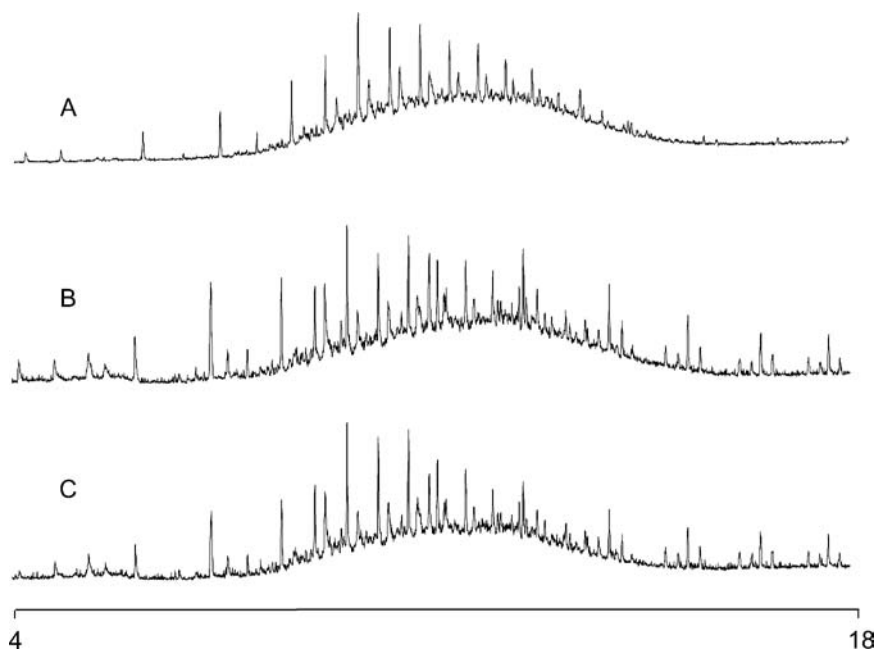


FIG. 8—Total ion chromatograms comparing three different 1997 military lots, Lot A-1 (A), Lot I (B), and Lot J (C). Lots I (B) and J (C) are indistinguishable.

based on the process oil. As for distinguishing between military lots and commercial sources, this may also be problematic. According to BAE SYSTEMS, they provide military-specification Composition C-4 to commercial manufacturers (A. Wilson, personal communication, 2004). Differences between Holston/BAE SYSTEMS and other manufacturers could be determined based on the use of DOS or DOA. Because Holston has used DOA in place of DOS since the 1980's, finding DOS plus a taggant (vapor detection agent) (24) would indicate that the Composition C-4 was manufactured at a facility other than Holston AAP (A. Wilson, personal communication, 2004).

## Conclusions

The process oils from U.S. military Composition C-4 and two commercial sources were analyzed by HTGC/MS to determine if military lots and commercial brands could be differentiated. Analysis of one M112 demolition block demonstrated that the oil is homogeneous throughout the block. Various lot numbers, encompassing 30+ years, were examined, and the oils could be differentiated in all but two lots. These two samples were from Composition C-4 with different lot numbers. Because of the procedure for assigning lot numbers, the same process oil may be in two different packaged lots, or different process oils may be in the same packaged lot. As a result, a forensic chemist attempting to associate blocks of Composition C-4 using the process oil may conclude: 1) process oils that are consistent may have originated from the same packaging lot number and 2) process oils that are different cannot be excluded as having originated from the same packaging lot number. This second conclusion, although not demonstrated in the data, is based on the information provided by the manufacturers. As a result of the production process, one packaging lot number of Composition C-4 may contain more than one lot of process oil. Also, if a sample of suspected Composition C-4 is analyzed, and it contains DOS (instead of DOA) plus a taggant, then the sample was not manufactured at Holston AAP.

## Acknowledgments

The authors would like to thank Andrew Wilson, Grady Dockery (both of BAE SYSTEMS Ordnance Systems, Inc.) and Brad Fly (Milan AAP) for their information on the production and packaging of Composition C-4 and John Goodpaster and Peter Dreifuss (both of ATF) for their technical advice. The assistance of ATF Special Agent Steven Beggs and members of ATF's Explosive Technology Branch in obtaining samples of Composition C-4 is also gratefully acknowledged.

## References

1. <http://holston-aap.com/hsaap/history.htm>, March 2004.
2. Composition C-4. United States Army-AR; 1963 Sept. Military Specification: MIL-C-45010A (MU).
3. Fedoroff BT, Sheffield OE. Encyclopedia of explosives and related items, PATR 2700, Vol. 3. Dover: Picatinny Arsenal, 1966;C484-8.
4. Polyisobutylene binder. Ordnance Corps; 1957 Jun. Military Specification: MIL-P-14536 (Ord).
5. Keto RO. Improved method for the analysis of the military explosive Composition C-4. *J Forensic Sci* 1986;31:241-9.
6. Peimer RE, Washington WD, Snow KB. On the examination of the military explosive, C-4. *J Forensic Sci* 1980;25:398-400.
7. Midkiff CR, Washington WD. Systematic approach to the detection of explosive residues. IV. Military explosives. *J AOAC* 1976;59:1357-74.
8. Keto RO. Analysis of the Eastern Bloc explosive Semtex-H. Proceedings of the Third Symposium on Analysis and Detection of Explosives; 1989 Jul 10-13; Mannheim-Neuostheim (Germany). Fraunhofer-Institut for Chemische Technologie, 1989;11-1-11-20.
9. Hobbs JR. Analysis of Semtex explosives. In: Yinon J, editor. Advances in analysis and detection of explosives. Netherlands: Kluwer Academic Publishers, 1993;409-27.
10. Buyten J, Duvekot J, Peene J, Mussche Ph. A capillary column for high-temperature gas chromatography. *Am Lab* 1991;13-8.
11. Brumley WC, Jones WJ, Grange AH. A survey of potential applications of high-temperature capillary gas chromatography for environmental analysis. *LC-GC* 1995;13:228-36.
12. van Lieshout HPM, Janssen HG, Cramers CA. Improvements in high-temperature PTV injection for HT-CGC. *Am Lab* 1995;38-44.

- [PubMed]
13. Tipler A, Johnson G. Optimization of conditions for high temperature capillary gas chromatography using a split-mode programmable temperature vaporizing injection system. *J High Res Chromatogr* 1990;13:365–70.
  14. Lawrence JF, Iyengar JR, Page BD, Conacher HBS. [Characterization of commercial waxes by high-temperature gas chromatography](#). *J Chromatogr* 1982;236:403–19.
  15. Barker A. The chromatographic analysis of refined and synthetic waxes. In: Adlard ER, editor. *Chromatography in the petroleum industry*. Amsterdam: Elsevier, 1995;55–93.
  16. Kuk RJ. Analysis of artificial fireplace logs by high temperature gas chromatography. *J Forensic Sci* 2002;47:1288–93.
  17. Giles JJ. The analysis of waxes and greases using high resolution gas chromatography. *J For Sci Soc* 1987;27:231–9.
  18. McCormack AJ, McCann JM, Bohler RJ. Determination of motor oil volatility using high-temperature gas chromatography. *LC-GC* 1991;9:28–32.
  19. Roehner RM, Fletcher JV, Hanson FV, Dahdah NF. [Comparative compositional study of crude oil solids from the Trans Alaska Pipeline System using high-temperature gas chromatography](#). *Energy and Fuels* 2002;16:211–7.
  20. Gallegos EJ, Fetzter JC, Carlson RM, Peña MM. High-temperature GC/MS characterization of porphyrins and high molecular weight saturated hydrocarbons. *Energy and Fuels* 1991;5:376–81.
  21. Speight JG. *The chemistry and technology of petroleum*. 3rd rev. ed. New York: Marcel Dekker, 1999.
  22. Ammunition lot numbering and ammunition data card. Picatinny Arsenal (NJ): U. S. Army TACOM-ARDEC; 1998 Jun. Department of Defense Standard Practice: MIL-STD-1168B.
  23. Ammunition manufacturers and their symbols. Rock Island (IL): U. S. Army Armament Munitions and Chemical Command; 1990 Nov. Military Standard: MIL-STD-1461E.
  24. Convention on the marking of plastic explosives for the purpose of detection. Montreal, Canada: International Civil Aviation Organization, 1991.

Additional information—reprints not available from author:  
 Michelle R. Reardon, M.S.F.S.  
 Bureau of Alcohol, Tobacco, Firearms and Explosives  
 Forensic Science Laboratory—Washington  
 6000 Ammendale Road  
 Ammendale, MD 20705-1250  
 E-mail: Michelle.Reardon@atf.gov