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Vacuum Collection of Gunpowder Residues from Clothing Worn by Shooting Suspects, and Their Analysis by GC/TEA, IMS, and GC/MS

ABSTRACT: Experiments were conducted to collect gunpowder (propellant) residues from shooters' clothing by vacuum and to analyze them by gas chromatography/thermal energy analyzer (GC/TEA), ion mobility spectrometry (IMS), and gas chromatography/mass spectrometry (GC/MS). The residues were collected on fiberglass and Teflon filters using the portable vacuum sampler, all supplied with the IMS instrument. Several solvents were examined for the extraction of the propellant components from the filters. The extracts were centrifuged and/or filtered, concentrated by evaporation, and analyzed without any additional clean-up procedure. Based on the results of the study, an operational method for analysis of gunpowder residues was introduced into casework without changing the present operational technique for gunshot (primer) residue (GSR) analysis on clothing implemented by the Israel Police. In the modified method, the clothing is first sampled by double-side adhesive-coated aluminum stubs (the tape-lift method) for GSR analysis (the existing method), followed by vacuum collection for propellant residue examination. The issue of interpretation of the analytical results is discussed.

KEYWORDS: forensic science, gunpowder residue, propellant residue, GC/TEA, IMS, vacuum collection

Numerous studies have been published on the analysis of propellant residues (1–12); however, only a few of them (3–7) proposed operational methods (which have also been implemented in casework) for sampling, detection, and identification of these residues on shooters and/or their clothing. Thus, in casework, sampling of gunpowder residues from skin surfaces, e.g., hands, face, or neck, is carried out by swabs moistened with organic solvents. The residues from clothing items are recovered by vacuum and collected on filters. Gunpowder residues are recovered from swabs and filters by solvent extraction, undergo clean-up procedures by solid phase extraction (SPE), and are then analyzed by various techniques.

Modern smokeless propellants for small arms ammunition almost exclusively contain nitrocellulose (NC) as the main explosive component (single-based). Other explosive ingredients may also be present, for example, glycerol trinitrate (nitroglycerine, NG) (double-based) or NG and nitroguanidine (triple-based) (7,12,13). Propellants also contain stabilizers such as diphenylamine (DPA) or ethyl centralite (EC), flash inhibitors such as 2,4-dinitrotoluene (2,4-DNT), and 2,6-dinitrotoluene (2,6-DNT) and plasticizers. Thus, analytical methods for the detection and identification of propellants or their residues are similar to those employed for the analysis of explosives or explosive residues in post-blast samples, e.g., GC/MS or GC/TEA.

In casework it is not a realistic scenario to apprehend a suspect immediately after a shooting incident; at best, he may be arrested several hours after the incident. Since gunpowder residues are lost from hands relatively fast, even without hand washing, the amounts of the residues that may be left on the shooters' hands several hours after shooting may be very small (normally in the nanogram levels and sometimes in the sub-nanogram levels) (4,6). Persistence of the propellant residues on the shooters' clothing is considerably longer than on his hands, resulting in a higher probability of their detection and identification. Thus the sensitivity of the analytical technique is a crucial factor in its applicability for the detection and identification of the gunpowder residues on suspects of shooting and their clothing. For instance, micellar electrokinetic capillary electrophoresis (MECE) with a diode array UV detector is not sensitive enough to be implemented in casework (8,9). To the best of our knowledge only two methods are used operationally for detection and identification of propellant residues on shooters' hands: high-performance liquid chromatography with a pendant mercury drop electrode detector (HPLC/PMDE) and GC/TEA due to their high sensitivities, e.g., between tens to hundreds of picograms for NG (4–7,14). It was reported that GC/MS may be sensitive enough for the examination of shooters' clothing (7). In recent years IMS technology gained widespread use for the detection of trace explosive evidence due to its portability, good sensitivity (comparable to GC/TEA), reasonable selectivity, and high speed of analysis (15). The selectivity may be increased by a combination of the GC and IMS methods (16). A very preliminary study for the applicability of IMS to detect propellant residues on shooters and their clothing was reported (17); however, the authors of the present research are not aware of any study resulting in the implementation of IMS for the above purpose in casework.

The casework methodology in the Israel Police regarding GSR (primer residue) examinations is to collect tape-lift (double-side adhesive-coated aluminum stubs) samples from hands, hair, and clothing of suspects or their belongings and analyze them by scan-

ning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) (18,19). Currently, no method is implemented in Israel for propellant residue analysis on suspects, their clothing, or belongings. It has been shown (18) that neither tape-lift nor vacuum sampling has a high recovery efficiency for GSR particles from clothing items, namely, about the same number of particles was recovered by applying two methods consecutively regardless of the order. It may be assumed that the same holds for propellant residue particles.

The objective of this work was to assess the applicability of the portable vacuum sampler, the fiberglass, and the Teflon filters supplied with the commercial IMS instrument for the collection of propellant residues from clothing items and their subsequent analysis by GC/TEA, IMS, and GC/MS. Four solvents were evaluated for the extraction of the residues from the filters. The samples were centrifuged and/or filtered, concentrated by evaporation, and analyzed without any additional clean-up steps. Based on the results of the study, an operational method for analysis of gunpowder residues was introduced into casework without changing the present operational technique for gunshot (primer) residue (GSR) analysis on clothing implemented by the Israel Police. In the modified method, the clothing is first sampled by double-side adhesive-coated aluminum stubs (the tape-lift method) for GSR analysis (the existing method), followed by vacuum collection for propellant residue examination.

Experimental

Materials

Explosive standards of NG, 2,4-DNT, and 2,6-DNT were obtained from Chem Service Ltd. PO Box 599, West Chester, PA at concentrations of 1000 μg/mL in acetonitrile. Also, aqueous solution of NG (1 mg/mL with 5% of dextrose) for I.V. infusions obtained from Taro Pharmaceutical Industries Ltd. Israel was used as a standard. In this case the solution was diluted in acetone and centrifuged (to remove the precipitate of dextrose) prior to use. All solvents in this study were of analytical grade. Standard working solution mixtures of NG, 2,4-DNT and 2,6-DNT in concentrations ranges of 1 to 20 ng/μL were prepared by dilution of standards in acetone. Also used were acetone solutions of the following compounds (prepared in a previous study (20)): 1,2 glycerol dinitrate (1,2-GDN), 1,3 glycerol dinitrate (1,3-GDN), 1 glycerol mononitrate (1-GMN), and 2 glycerol mononitrate (2-GMN).

Analytical Equipment

GC/TEA—A GC (Hewlett Packard, Model 6890), equipped with an (SGE Scientific) injector was used. Most of the experimental work was conducted with a 100% dimethyl polysiloxane fused silica capillary column (Rtx-1) 30 m long, 0.25-mm internal diameter, and a 0.25-μm film thickness. The carrier gas was helium at a head flow 2 mL/min (22 psi). The injector port temperature was 175°C. The oven temperature was held at 75°C for 1 min, ramped at 20°C/min to 200°C, then at 40°C/min to 250°C and then held at 250°C for 7 min. The detector was a TEA analyzer (Thermo Electron, Model 543). The interface temperature was 300°C, and the pyrolyzer temperature was 850°C. The injected samples were 1 to 10 μL in splitless mode. Some of the experiments were conducted with the same column with a 15-m length. The carrier gas was helium at a head flow 1 mL/min (22 psi). The injector port temperature was 175°C. The oven temperature was held at 60°C for 2 min, ramped at 35°C/min to 145°C, held at this temperature for 1 min, ramped at 35°C/min to 220°C, and then held at 220°C for 2 min.

IMS—IONSCAN® MODEL 400A of the Barringer Instruments Inc., U.S.A. The system consists of the IMS analyzer and portable vacuum sampler. Two types of filters were used in the study, Teflon and fiberglass. The diameter of the filters was 3 cm, and the diameter of the sampling area 2 cm. According to the manufacturer, the volumetric flow obtained by the vacuum sampler is approximately 30 to 40 L/min through the Teflon filters and 50 to 60 L/min through the fiberglass filters. The Teflon filters are classified as 50-μm pore size filters for air flow; however, for particles it is closer to a 3-μm filter in air flow of 30 to 35 L/min. Particles get trapped due to a complex path within the filter. Fiberglass filters have poor collection efficiency for particles below 40-μm size. Figure 1 shows the SEM micrographs of the filters. In the analyses by IMS in this study, a few microlitres of the solutions obtained from the extracted filters (see below) were placed on the fiberglass or Teflon filter and processed as follows: the IMS was operated in the mode for explosives detection with operating conditions as follows: tube temperature: 107°C, inlet temperature 240°C, desorber temperature: 225°C, desorption time: 6.8 s, drift flow 400 mL/min and sample flow 200 mL/min.

GC/MS—Two instruments were used as follows:

a) A GC (Varian, Model 3400) equipped with an (SGE Scientific) injector was used. The 100% dimethyl polysiloxane fused silica capillary column (BP-1) was 30 m long, with a 0.25-mm internal diameter and a 0.25-μm film thickness. The carrier gas was helium at a head flow of 0.5 mL/min. The injector port temperature was 170°C. The oven temperature was held at 100°C for 3 min, ramped at 10°C/min to 250°C, and then held at 250°C for 3 min. The detector was MS with Ion Trap (Varian, Model Saturn 2000). The interface temperature was 170°C. The injected sample was 1 μL in splitless mode.

b) An Agilent MSD, Model 5973N, coupled to an Agilent 6890 PLUS GC. The GC column was J&W 5% phenyl equivalent polysilphenylene-siloxane fused silica, capillary column (DB-5MS) 15 m long, 0.25-mm internal diameter, and a 0.25-μm film thickness. The carrier gas was helium at a head flow of 1.5 mL/min (17.9 psi). The injector port temperature was 180°C. The oven temperature was 60°C, which was ramped at 25°C/min to 280°C. The transfer line was held at 180°C. Ion source temperature was 180°C and quadrupole was at 150°C. Scan rate was 3.11 scans/s. Electron energy was 70 eV. The injected sample was 3 μL in splitless mode.

Both GC/MS instruments were not optimized (regarding the sensitivity) for the analysis of gunpowder components.

Shooting Experiments and Sampling of Gunpowder Residues

All firing tests were carried out in an indoor shooting range, using a 9-mm FN semiautomatic pistol held in both hands and with 9-mm Winchester Super X ammunition (except if stated otherwise). The ventilation in the range was turned off during the experiments. The shooters wore various types of clothing (laboratory coat—cotton; shirt—65% polyester, 35% cotton; sweater—acrylic/wool knit 70:30). One round or more was fired. The shooter's clothing was sampled for gunpowder residues at different time intervals (5 min, 1 h, 2 h, 3 h, 4 h, and 6 h) after firing. Only the 5-min interval was tested for all the three clothing items mentioned above. Every other time interval (from the list) was tested for only one clothing item chosen at random from the above three items. In some of the experiments more than one sample was collected from the clothing item, e.g., one sample from the right area of the item and one sam-

ple from the left area. Altogether eight shooting experiments of one round were carried out to assess the applicability of the three methods, GC/TEA, IMS, and GC/MS to detect gunpowder residues in samples from the shooter's clothing and collected at different time intervals after discharge. Between firing and sampling, the subjects carried out their usual work in the laboratory (in an area not exposed to firearms discharge residues). The sampling was carried out with the Barringer IMS portable vacuum sampler using one of the two types of filters. Most of the experiments were conducted with fiberglass filters. Various sampling times (up to 6 min) were examined. The clothing items were also sampled as blanks before shooting.

In some of the experiments a particular area of the clothing was first sampled by a double-side adhesive-coated aluminum stub (18) and then by vacuuming. Clothing items from five real shooting cases were also sampled for propellant residues after they were sampled by the tape-lift method for the examination of primer residues.

The two types of filters were also used concurrently in the filter holder (fiberglass filter first) to examine the extent of the propellant residue loss by using the fiberglass filter as compared to the Teflon filter. In this experiment, the shooter fired consecutively four rounds of different ammunitions (Winchester, TZZ, CCI, and Federal), and his clothing (sweater: acrylic/wool knit 70:30) was sampled immediately after firing.

Extraction of Propellant Residues from Filters and Their Analysis

Four solvents (acetone, methylene chloride, ethyl acetate, and chloroform) were examined for the extraction efficiency of the propellant constituents from the filters as follows: several microlitres of the standard working solution mixtures were placed on the filters and dried for about 2 min at room temperature. The filters were placed in the 1.1-mL cylindrical glass vials to which 1.0 mL of a solvent was added. The vial was sonicated for 5 min. The solution was decanted to another 1.1-mL vial, and the filter was rinsed with an additional 0.5 mL of the solvent. The combined volume was finally concentrated to about 100 μL in the same vial or to about 20 μL after transfer to a 0.5-mL conical vial using a stream of dry nitrogen. A similar procedure was applied when processing filters that were used for vacuum sampling of gunpowder residues from clothing items in shooting experiments. In this case a centrifugation step was added after the sonication, and if the decanted solution still looked turbid it was filtered through a 0.45-μL filter. No additional cleanup step was employed. The solutions obtained were analyzed by GC/TEA, IMS, and GC/MS. Normally the analyzed aliquot was about 10% of the final concentrate volume. The extraction efficiency was assessed using the results obtained by GC/TEA. The residues in the spent cartridge cases of the ammunition used in the shooting experiments were also analyzed by the three techniques for comparison. Since methylene chloride and the Teflon filters were finally chosen for casework examinations (see next paragraph), experiments were carried out to assess the effect of the garments fibers (cotton and acrylic/wool knit) on the recovery of the propellant components in the extraction procedure. For this purpose, the clean clothing was first vacuumed for 2 min. The filter was then spiked with 10 μL of a standard solution containing 10 ng/μL of NG, 2,4-DNT, and 2,6-DNT. The subsequent extraction procedure was the same as described above with the addition of the centrifugation step.

Results and Discussion

The approximate limits of detection (LOD) of the GC/TEA and the IMS employed in the study for NG, 2,4-DNT and 2,6-DNT are shown in Table 1. The considerably lower sensitivity of GC/TEA

for NG compared to DNT is due to the thermal decomposition of NG in GC columns (20), leading to high nonlinearity of the NG peak heights as a function of concentration, in particular approaching the LOD. This phenomenon was more pronounced when using the 30-m column compared to the 15-m length column. Furthermore, when using the 30-m column, in most of the chromatograms the NG peak (Fig. 2*a,* Peak A2) was preceded by a smaller peak (Fig. 2*a,* Peak A1) that could be identified as 1,2-GDN (one of the possible thermal decomposition products of NG) based on the analysis by GC/TEA of the synthesized lower nitrate esters of glycerol

TABLE 1—*Approximate LOD (ng) of the propellant components in GC/TEA and IMS.*

	NG	2,4 DNT	2,6 DNT
GC/TEA 15-m length column	0.2	0.05	0.05
GC/TEA 30-m length column	0.5–1.0	0.1	0.1
IMS*	0.3	0.3	0.3

*Every component alone on both types of filters (see text).
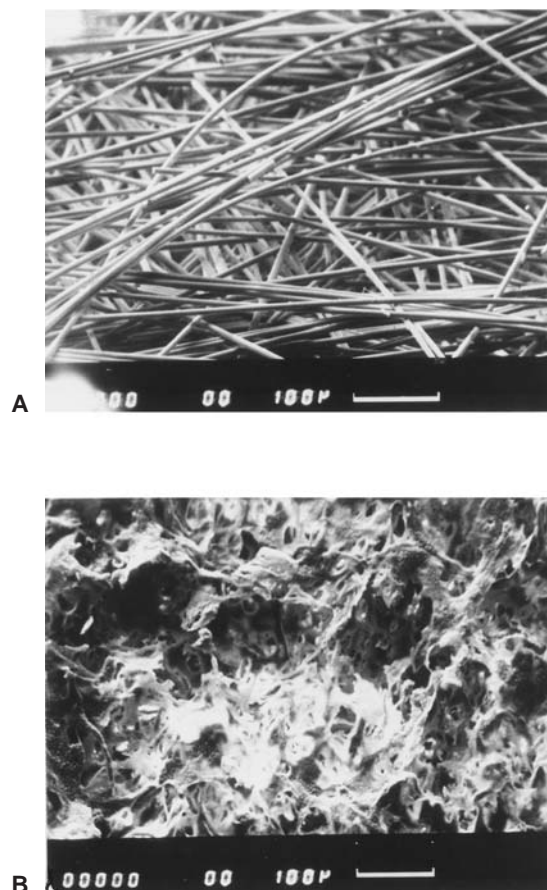

A

B

FIG. 1—*SEM micrographs of the Barringer filters for the portable vacuum sampler: (a) fiberglass filter, (b) Teflon filter.*
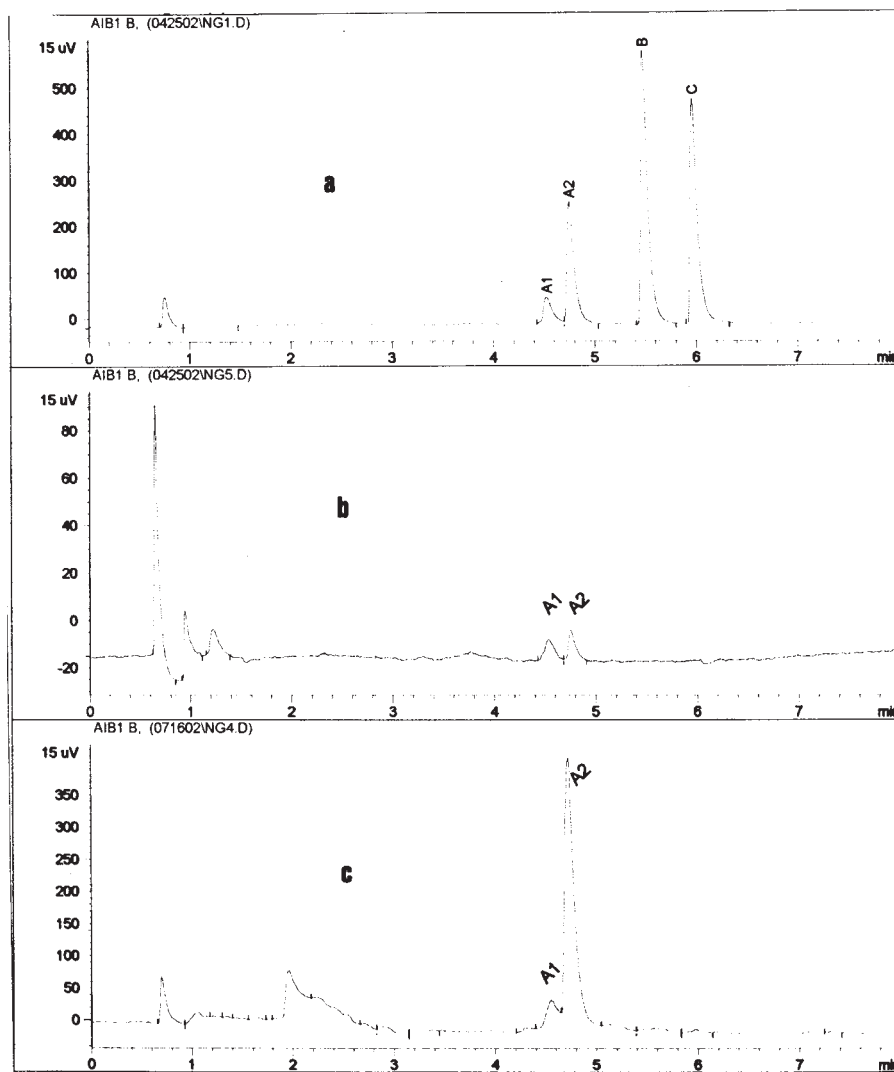
FIG. 2—*GC/TEA chromatograms (30-m column) of various samples (see text): (a) sample of a standard solution containing 10 ng of NG (Peaks A1 and A2), 10 ng of 2,6-DNT (Peak B) and 10 ng 2,6-DNT (Peak C); (b) sample collected from a shooter's cotton shirt 6 h after firing one round; (c) sample collected from a glove from a casework.*

(20). This smaller peak could hardly be detected when using the 15-m length column. Figure 3 shows the GC/TEA chromatograms of 1,2-GDN, NG, and 1,3-GDN. A match in retention times of the smaller peak in the chromatogram of NG and the peak of 1,2-GDN can be seen. Spiking of the NG solution with the solution of 1,2-GDN increased the intensity of the smaller peak. The relative intensity ratio of the two peaks related to NG was not constant, and they were not always well separated (Fig. 4). Sometimes an additional broad peak was measured (Fig. 4, Peak A0), which could also be related to the thermal decomposition of NG and might be identified as 2-GMN. On one hand, the thermal decomposition is a drawback, decreasing the sensitivity to NG, but, on the other hand, the presence of the two (or more) chromatographic peaks related to NG increases the probability of its identification by GC/TEA.

As may be seen in Table 1, the sensitivity of the IMS to the three propellant components is similar to the GC/TEA. However, when these components are in a mixture (with the same weight concentrations), most of the time only NG is detected and not the DNT isomers. In such a situation, detection of the DNT isomers is ob-

tained when their quantity is at least 10 to 20 ng. Furthermore, no reliable discrimination between 2,4-DNT and 2,6-DNT is obtained by the IMS.

The principles of IMS (15) will be described here briefly to understand the obtained results. The instrument consists of two main areas: the reaction region and the drift region. In the reaction region, the atmospheric pressure carrier gas (purified air), the reactant gas (hexachloroethane), and an internal calibrant (4-nitrobenzonitrile) are ionized by a ^{63}Ni beta emitter to form Cl^- ions. The reactant ions can then undergo one or more ion/molecule reactions with the analyzed material, e.g., electron attachment, proton abstraction, and chloride attachment. Thus, some analyzed materials may form several ionic species. The various ions migrate in the drift region, where an electric field gradient is applied and are separated according to their mobility (drift time). The obtained mobility spectrum is called *plasmagram.*

The plasmagrams were analyzed automatically by the programmed algorithm in the Barringer IMS. As explained above, some explosives may have several peaks in the plasmagram, e.g.,

NG (3 peaks) (Fig. 5), RDX, and PETN (4 peaks); others may have only one peak, e.g., 2,4-DNT and 2,6-DNT (Fig. 6). Figure 6*a* shows a plasmagram of 20-ng 2,4-DNT. The plasmagram indicated detection of the two isomers, although only 2,4-DNT was present. This is probably due to very close drift times of the two isomers, as may be seen in the figure, resulting in a poor discrimination. Figure 6*b* shows plasmagram of 20 ng of 2,6-DNT. This time only 2,6-DNT was detected as should be. The label "cal" in a plasmagram refers to the internal calibrant, and the label "contam" refers to several materials excreted in sweat, which contribute peaks in a plasmagram and are labeled by the system. When the amount of the analyzed explosive is too small and/or there are too many interfering materials, there is a high probability that not all the peaks of the explosive will be detected. Clearly, the probability of identification of a compound increases with the number of the detected peaks. Thus, the inherent potential for identification of NG by IMS is higher than that of 2,4-DNT or 2,6-DNT. According to the operation algorithm of the instrument, there may be two levels of detection: (a) "positive"—meaning detection of at least two from several peaks for explosives having several peaks. Such detection will be marked by the instrument as "Alarm." "Alarm" also will be marked for detection of one peak for explosives having only one peak. (b) "Optional"—meaning detection of only one of the peaks of those explosives having several peaks. In such a situation there will be no "Alarm," and clearly it means less probable identification.

There is a difference between the two types of filters regarding the thermal desorption of a sample. It was found that there was a complete desorption of a sample in one analysis cycle when a fiberglass filter was used as the substrate. When using the Teflon filter, NG always was desorbed in the first analysis cycle, while, for the DNT isomers, often there was a need for an additional analysis cycle for a complete desorption. As a matter of fact, Barringer Inc. recommends using fiberglass filters for desorption and not Teflon filters for explosive trace analysis.

The approximate LOD of the two GC/MS instruments for the three gunpowder components were in the order of several nanograms. As mentioned above, their operating conditions were not optimized for maximum sensitivity with respect to the propellants' components. The composition of gunpowder in the Winchester ammunition (the main ammunition used in the study) (as an-
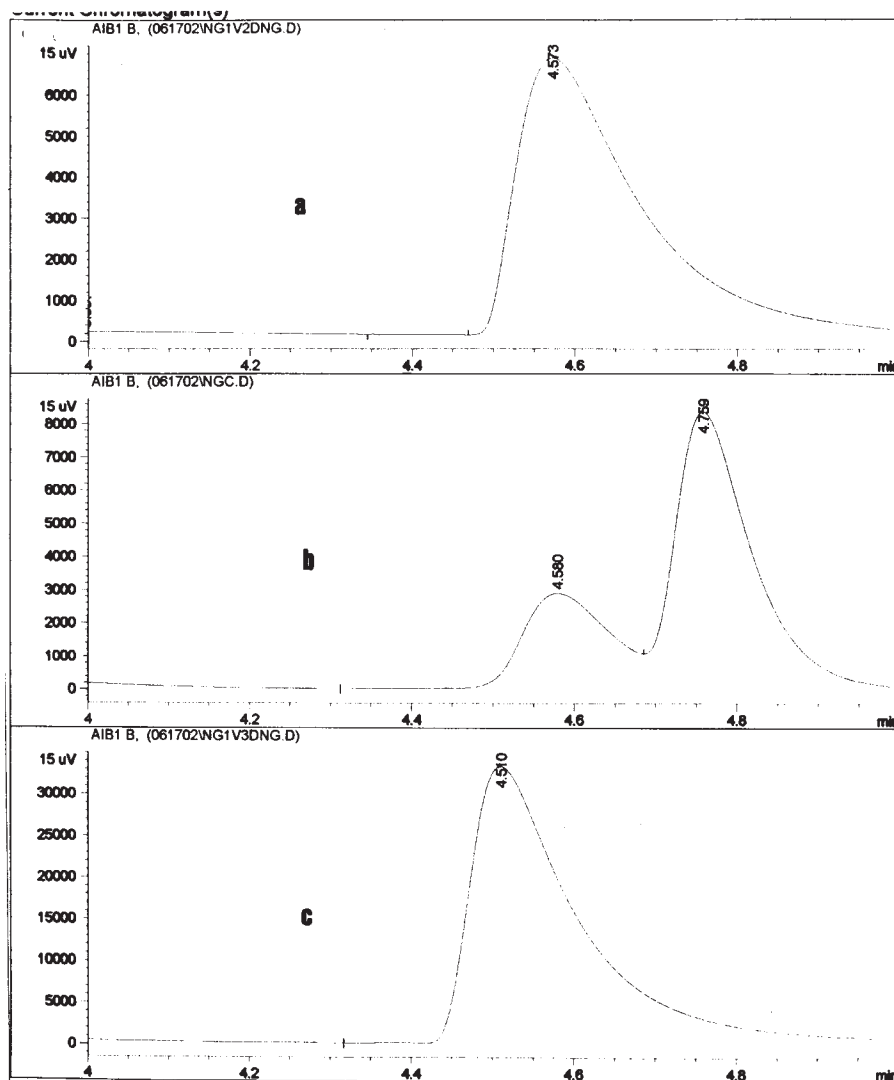

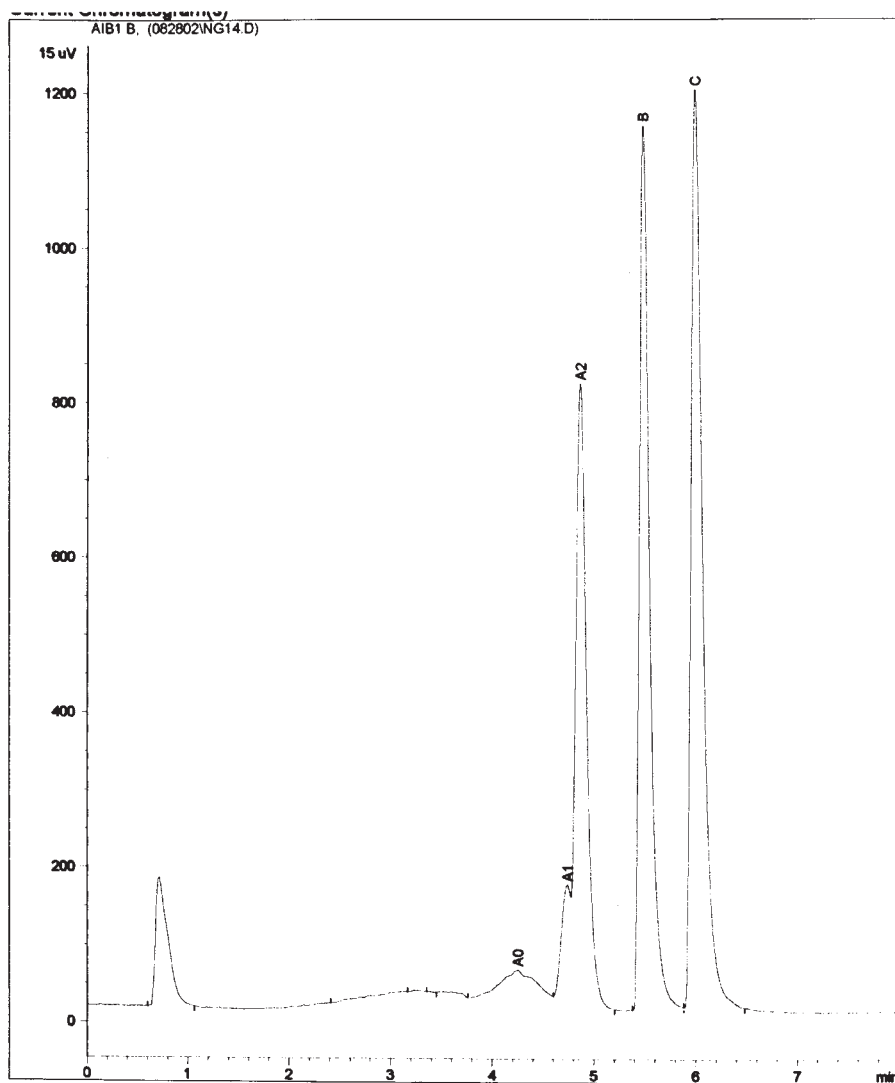FIG. 3—*GC/TEA chromatograms (30-column) of three standard solutions: (a) 1,2-GDN; (b) NG; (c) 1,3-GDN.*

FIG. 4—*GC/TEA chromatogram (30-m column) of a different (from Fig. 2a) standard solution containing the three components and obtained in a different time (see text).*
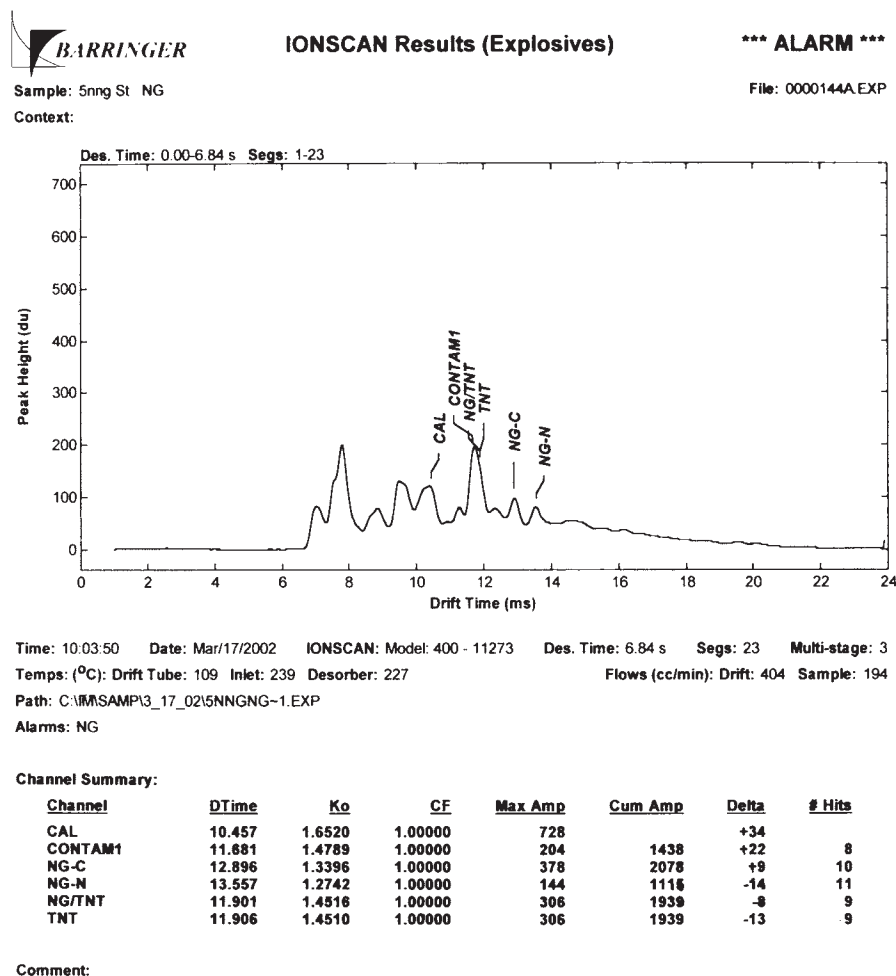
BARRINGER   **IONSCAN Results (Explosives)**   *** **ALARM** ***

Sample: 5nng St NG   File: 0000144A.EXP

Context:

Time: 10:03:50   Date: Mar/17/2002   IONSCAN: Model: 400 - 11273   Des. Time: 6.84 s   Segs: 23   Multi-stage: 3

Temps: (°C): Drift Tube: 109   Inlet: 239   Desorber: 227   Flows (cc/min): Drift: 404   Sample: 194

Path: C:\IM\SAMP\3_17_02\5NNGNG~1.EXP

Alarms: NG

Channel Summary:

Channel	DTime	Ko	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.457	1.6520	1.00000	728		+34	
CONTAM1	11.681	1.4789	1.00000	204	1438	+22	8
NG-C	12.896	1.3396	1.00000	378	2078	+9	10
NG-N	13.557	1.2742	1.00000	144	1115	-14	11
NG/TNT	11.901	1.4516	1.00000	306	1939	-8	9
TNT	11.906	1.4510	1.00000	306	1939	-13	9

Comment:

FIG. 5—*Plasmagram of a standard solution containing 5 ng of NG.*

alyzed by GC/MS) was as follows: NG, 2,4 DNT, 2,6 DNT, diphenyl amine (DPA), ethyl centralite, dinitro-DPA, and nitroso-DPA. The concentration of NG was by far much higher than the other constituents, not taking into account NC, which could not be analyzed by GC/MS. Furthermore, NG was the major component in the propellant of the three other ammunitions used in the study.

No significant differences in the extraction efficiency of the propellants components from the filters by the four tested solvents had been found. The obtained results were highly variable (the highest variability for NG) for the same solvent, ranging from 30 to 100%. Such high variability may be attributed at least partially to the relatively low precision of the GC/TEA method, in particular for NG due to its thermal decomposition. Finally, methylene chloride was chosen for shooting experiments and casework exhibits due its advantage of not dissolving nitrocellulose (10). Since nitrocellulose is not sufficiently volatile for GC analysis (21), its introduction (as a major component of propellants) to the GC column may accelerate the deterioration of its performance. No significant difference was found in the recovery of NG, 2,4-DNT, or 2,6-DNT from the Teflon filters covered by the tested garment fibers. The obtained recovery was quite variable and found to be in the range of 30 to 70%.

It appeared that 2 min was sufficient time to sample gunpowder particles from a shirt with long sleeves or from a sweater quite efficiently (70 to 90% collection efficiency) using the Barringer portable vacuum sampler. Accordingly, larger areas will need more time.

In nine out of ten collected samples from shooting experiments and in three out of five examined real shooting cases, NG was detected by GC/TEA. All the blank samples collected from clothing prior to firing tests were negative for NG. Two of the NG positive cases were also positive for primer (GSR), and one negative for NG was positive for primer (GSR). It should be noted again that all the clothing exhibits from casework were first sampled by the tape-lift method for primer residues (GSR) prior to vacuum sampling for propellant residues. Figure. 2b shows the chromatogram of a sample collected 6 h after shooting. It may be seen that two peaks related to NG appear, matching those in the standard (Fig. 2a). Figure 2c shows the chromatogram of a sample collected from a glove, one of the exhibits from a real case. Again two peaks related to NG show up as in the standard. DNT isomers were detected only in few samples collected immediately after the shooting. As was already mentioned previously, the concentration of the DNT isomers in the tested ammunition was very low compared to that of NG.
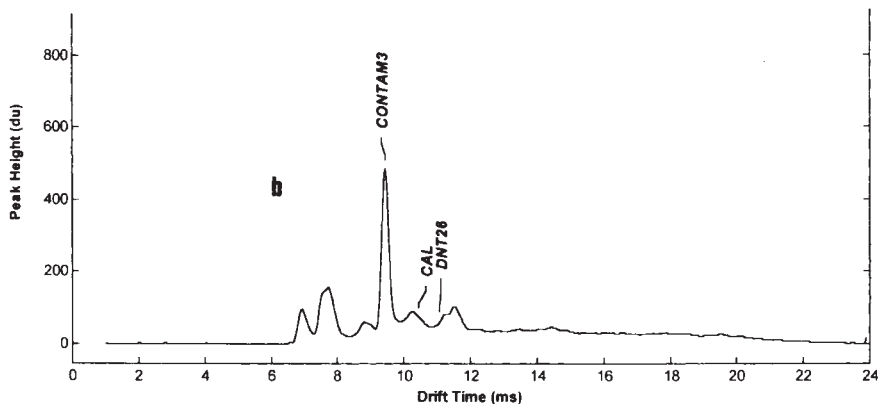
In the experiments in which the two types of filters were used concurrently in the filter holder, it was found that about 60% of gunpowder particles were collected by the fiberglass filter and the rest by the Teflon filter. This clearly indicates that it is beneficial to use the Teflon filters for collection of propellant residues, contrary to the Barringer Inc. recommendation to use the fiberglass filters for trace explosive analysis. However, as already discussed above,

FIG. 6—*Plasmagrams of the following standards solutions: (a) 20 ng of 2,4-DNT, (b) 20 ng of 2,6-DNT.*

this recommendation relates to using the same filter for collection and analysis without further processing as was done in this study.

The majority of samples (in shooting experiments and in casework) that were positive for NG by GC/TEA exhibited only one peak related to NG in the IMS plasmagrams. Only samples collected 5 min after firing gave two or three peaks resulting in "Alarm." A one-peak plasmagram for NG does not necessarily indicate a small amount of NG. There were samples from shooting experiments in which the amount of NG (according to the GC/TEA analysis) was much higher than its LOD by the IMS, but the plas-

magram had only one peak of NG. This behavior was different from what was observed for the standard solutions containing NG and the two DNT isomers. Apparently, it may be attributed to various interferences present in the real life samples (22). An example for this phenomenon is demonstrated by the samples from two cases as follows: One sample collected from a glove gave a high peak of NG in the GC/TEA chromatogram (Fig. 2c). However, the IMS analysis of the sample that was run in duplicate resulted in one plasmagram having one peak related to NG (Fig. 7a) and the second plasmagram without any peak of NG (Fig. 7b). As may be

seen, these results also demonstrate quite a high variation in the patterns of plasmagrams that may be obtained from the same sample. The other sample collected from a shirt gave a relatively small peak of NG in the GC/TEA chromatogram (Fig. 8). The plasmagram of the sample exhibited two peaks related to NG (Fig. 9), resulting in "Alarm" for NG. It may be assumed that a combination of GC and IMS would have provided a better discrimination and a higher probability of identification than IMS alone (16,22).

Samples having relatively high NG concentrations as was elucidated by GC/TEA were also analyzed by GC/MS. However, only samples collected 5 min after shooting resulted in the identification of NG and DNT by GC/MS. Not one of the casework examples tested (where NG was identified by GC/TEA) could be confirmed by GC/MS. As was mentioned previously, the two GC/MS were not optimized for the analysis of explosives.

As was shown, in most of the shooting experiments and in some of the casework samples, detection and identification of NG by GC/TEA was also accompanied by detection of at least one peak related to NG by IMS. The question may be asked if this is sufficient for what is called "positive identification" or "confirmation of identification" of NG in those samples. "In general, the question of which and how many techniques are required for con-

Des. Time: 0 00-6 84 s   Segs: 1-23
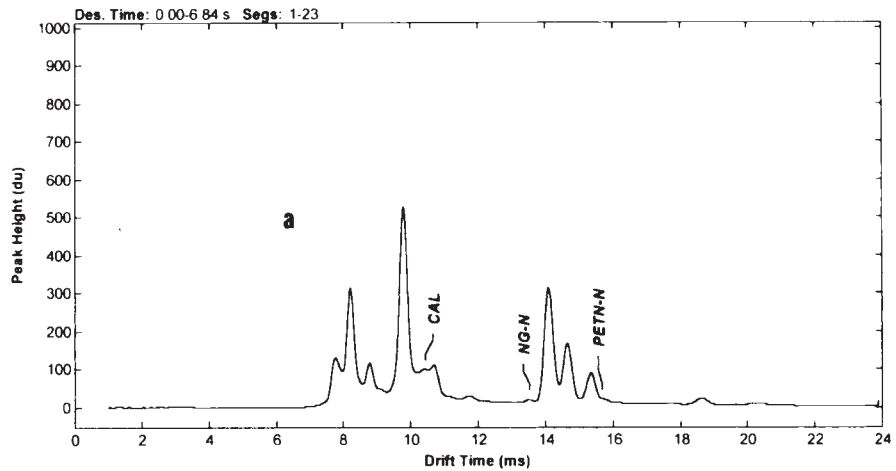
Time: 13:46:34   Date: Jul/23/2002   IONSCAN: Model: 400 - 11273   Des. Time: 6.84 s   Segs: 23   Multi-stage: 3
Temps: (°C): Drift Tube: 109 Inlet: 239 Desorber: 226   Flows (cc/min): Drift: 402 Sample: 194
Path: C:\IM\SAMP\7_23_02\SAMPLE4.EXP
Alarms:

Channel Summary:

Channel	DTime	Ko	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.439	1.6520	1.00000	709		+25	
NG-N	13.534	1.2742	1.00000	121	286	-19	4
PETN-N	15.677	1.1000	1.00000	48	128	+17	4
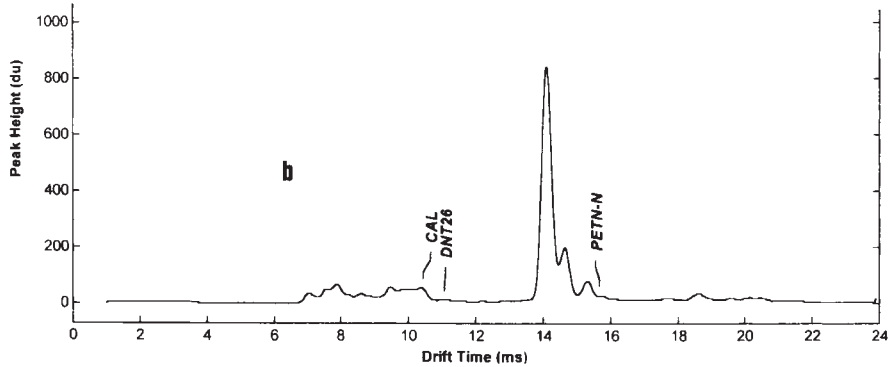
Time: 14:32:39   Date: Jul/23/2002   IONSCAN: Model: 400 - 11273   Des. Time: 6.84 s   Segs: 23   Multi-stage: 3
Temps: (°C): Drift Tube: 109 Inlet: 239 Desorber: 225   Flows (cc/min): Drift: 402 Sample: 218
Path: C:\IM\SAMP\7_23_02\2424F.EXP
Alarms: DNT

Channel Summary:

Channel	DTime	Ko	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.442	1.6520	1.00000	624		+29	
DNT26	11.072	1.5580	1.00000	46	83	-8	2
PETN-N	15.682	1.1000	1.00000	50	99	+32	3

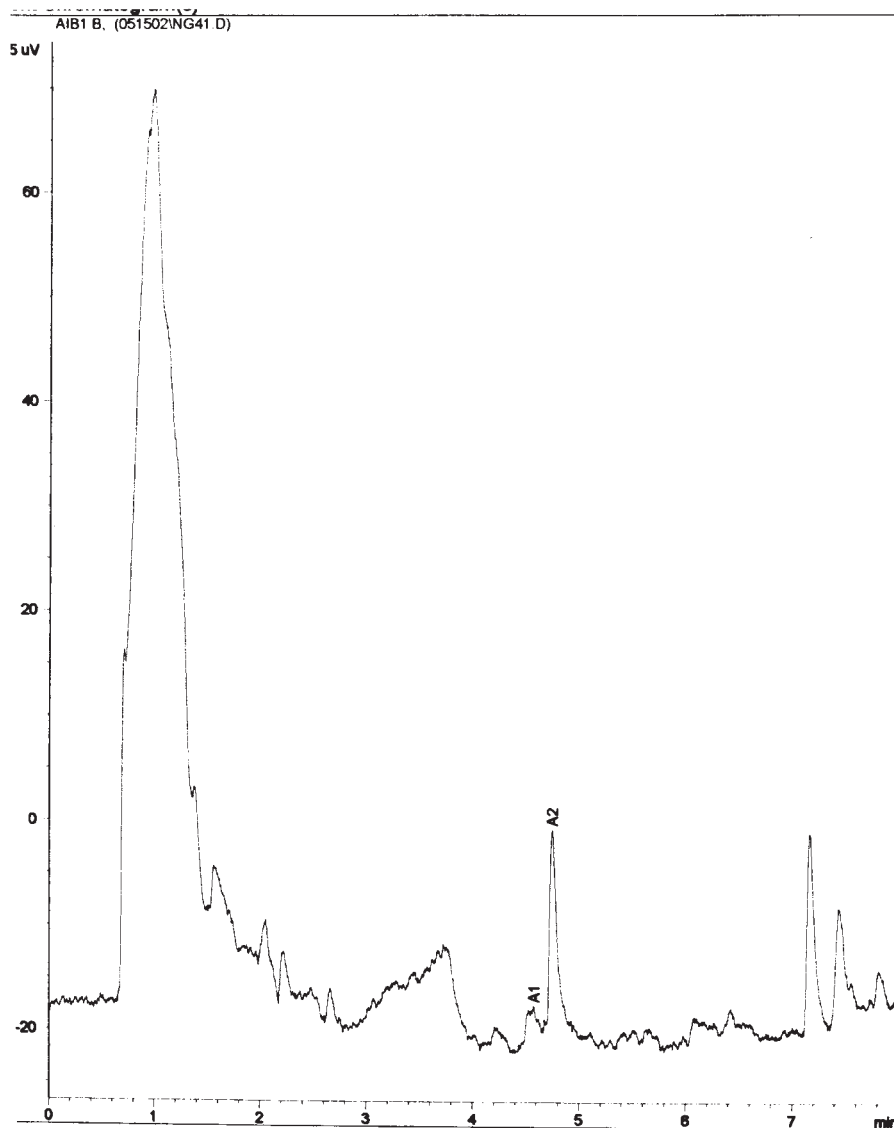FIG. 7—*Two plasmagrams of the same sample shown in Fig 2c.*

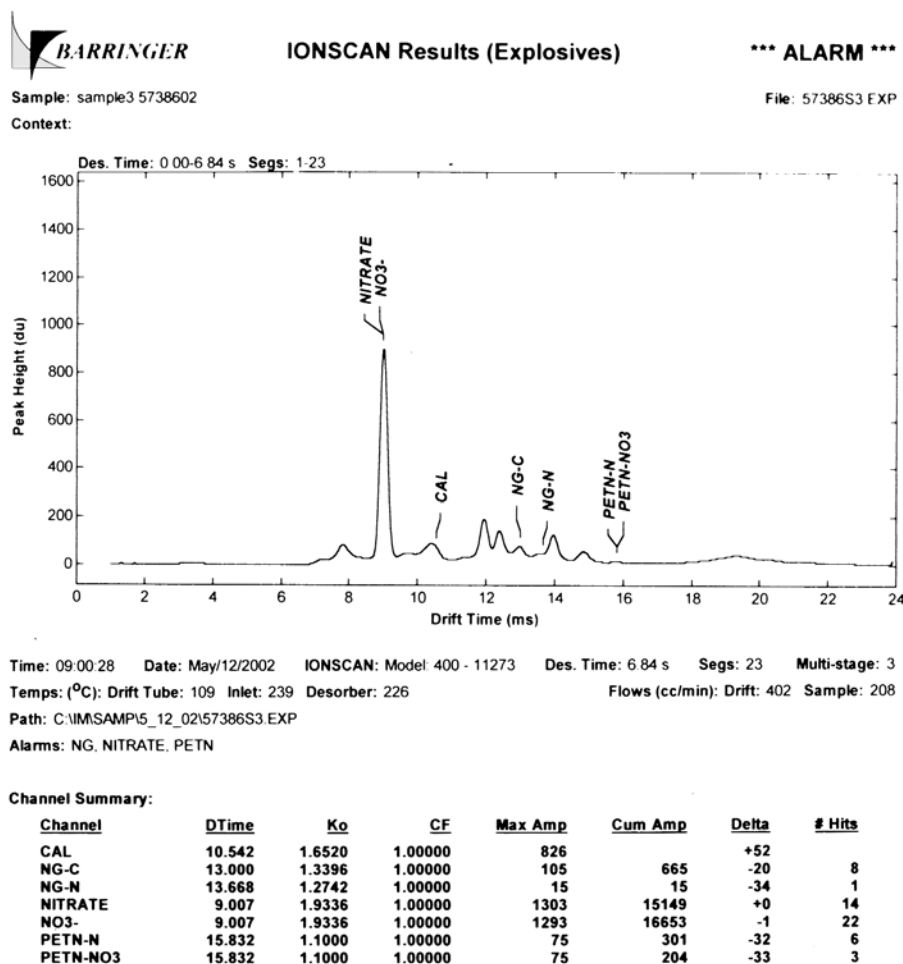FIG. 8—*GC/TEA of a sample collected from a casework shirt.*

FIG. 9—*Plasmagram of the sample shown in Fig. 8.*

firmation of identification of an explosives trace is complicated, and there is no single answer" (23). Although comprehensive identification by MS would be a method of choice, it is not sensitive enough in many real life cases. There seems to be a consensus among experts that at least two orthogonal methods are necessary for this purpose. Thus, the Forensic Science Service, UK, uses HPLC/PDME and GC/TEA for that purpose (6), and the Forensic Explosives Laboratory, DERA, UK, uses three different GC/TEA systems (23).

As was shown in our study, the identification of NG by GC/TEA (using a 30-m column) is characterized by two close peaks in the chromatogram due to the thermal decomposition of NG. Although this phenomenon decreases the sensitivity of the method, it has the advantage of increasing the probability of identification using one GC/TEA system. Such a result supported by the IMS analysis may, in our view, form the basis for the following interpretation: "firm indication for the presence of NG in the sample." Clearly, the weight of evidence linking a suspect to firearms will be increased if the tape-lift sample from the same exhibit would be also positive for GSR.

Conclusion

Results of the study show that it is feasible to use the IMS portable vacuum sampler to collect gunpowder residues from the clothing of suspects of shooting after it was sampled by the tape-lift method for primer residues (GSR). GC/TEA and IMS are sensitive enough to detect and identify gunpowder residues in real life samples. Formation of two peaks related to NG in the GC/TEA chromatograms increases the probability of its identification by this method.

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