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A Novel Method for Extraction and Analysis of Gunpowder Residues on Double-Side Adhesive Coated Stubs

ABSTRACT: A study was conducted to develop an efficient method for extraction and analysis of gunpowder (propellant) residues from double-side adhesive coated stubs, which are used for sampling suspects or their clothing for gunshot (primer) residues (GSR). Conductive and non-conductive double-side adhesives were examined, and the analysis was carried out by gas chromatography/thermal energy analyzer (GC/TEA) and ion mobility spectrometry (IMS). The optimal procedure for the extraction, as was developed in the present study, employs two stages: (1) extraction of the stubs with a mixture of 80% v/v aqueous solution of 0.1% w/v of sodium azide and 20% v/v of ethanol employing sonication at 80°C for 15 min. and (2) residues from the obtained extract were further extracted with methylene chloride. The methylene chloride phase was concentrated by evaporation prior to analysis. Extraction efficiencies of 30–90% for nitroglycerine (NG) and for 2,4-dinitro toluene (2,4-DNT) were found. No significant interferences in the analysis were observed from the adhesives or skin. Interferences were observed in the analysis by the GC/TEA of the samples collected from hair. The method enables analysis of propellant residues on a double-side adhesive coated stub after it was examined for primer residues by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX). Thus, the probative value of the evidence may be increased.

KEYWORDS: forensic science, gunpowder residue, propellant residue, GSR, GC/TEA, IMS, SEM/EDX

Numerous terror activities as well as many serious criminal offenses involve firearms. Detection and analysis of gunshot (primer) residues (GSR) and/or gunpowder (propellant) residues on a suspect may link him to such an incident (1–3). Obviously, finding both types of residues (primer and propellant) may have a higher probative value than finding only one type.

SEM/EDX is a well-established method for detection and analysis of GSR on double-side adhesive coated aluminum stubs used to sample a suspect, his clothing, or his belongings and is used by most the forensic labs in the world. This method, however, has some drawbacks:

1. It is quite slow even when using an autosearch system.
2. It has a relatively low “success” rate of detection (about 10%) (4,5).
3. Not all primer residues are considered unique to discharge of firearms.
4. There is a low variability in compositions of primers.

Numerous studies have been published on the analysis of propellant residues (1,2), however only a few of them (4,6,7) 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. Gunpowder residues are recovered from swabs by solvent extraction, undergo

clean-up procedures by solid phase extraction (SPE), are concentrated by evaporation, and are analyzed by two techniques: 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 pg for NG. Primer residues are recovered from the swabs by filtration and analyzed by SEM/EDX. A considerably higher “success” rate of detection in casework was reported for gunpowder residues than for primer residues (4). Propellant residues from clothing items are collected by vacuum or filters. After solvent extraction, they are analyzed either by HPLC/PMDE and GC/TEA (4,6) or by GC/TEA and ion mobility spectrometry (IMS) (7).

The swab method to collect primer and gunpowder residues has not been adopted world-wide, in spite of its potentially higher evidential value, and as was pointed out, most of the forensic labs examine only primer residues on double-side adhesive coated stubs used for sampling shooting suspects. It is reasonable to assume that an operational method to analyze propellant residues in combination with primer residues on the stubs would encourage at least some of the labs to adopt analysis of both types of residues. Micellar electrokinetic capillary electrophoresis (MECE) with a diode array UV detector was studied to analyze propellant residues on adhesives, but it appears that it is not sensitive enough to be implemented in casework (8). Another disadvantage of the MECE method lies in the fact that the adhesive had to undergo preliminary pretreatment (extraction of components, which may interfere in the analysis of propellant residues) before its application for collection of primer and gunpowder residues.

The objective of the present study was to develop an efficient method for extraction and analysis of gunpowder residues on the double side adhesive coated stubs, which are presently used for collection of primer residues. The method should be applied after the examination of primer residues (GSR). The major problem in

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achieving this goal is minimizing co-extraction of adhesive and skin debris components, which interfere in the analysis of propellant residues. Some organic solvents were tried, as well as water and water/ethanol mixtures (4,9–11).

Experimental

Materials

Explosive standards of NG, 2,4-DNT, and 2,6-DNT were obtained from Chem Service Ltd.² at concentrations of 1000 µg/mL in acetonitrile. Also, an 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. Aqueous solutions were prepared from de-ionized water. Standard working solution mixtures of NG, 2,4-DNT, and 2,6-DNT in concentrations of 1–10 ng/µl were prepared by dilution of standards in acetone.

Twenty-five mm aluminum stubs coated with 3M Scotch Tape No. 465 (used in the Israel Police for standard SEM/EDX examinations including GSR) or with one of the two types of conductive double side adhesive tapes (Agar Scientific Ltd. and SPI supplies) were used in the experiments.

Analytical Equipment

A GC (Hewlett Packard, Model 6890), equipped with an (SGE Scientific) injector was used. A 100% dimethyl polysiloxane fused silica capillary column (Rtx-1) 30 m long, 0.25 mm internal diameter, and 0.25 µm film thickness was used in the study. The carrier gas was helium at a head flow of 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 2 µL in splitless mode.

IMS—IONSCAN® MODEL 400A of the Barringer Instruments, Inc. consists of the IMS analyzer and portable vacuum sampler. The principles of IMS are described briefly, and more details on the technique may be found elsewhere (7,12). The instrument consists of two main areas: the reaction region and the drift region. In the reaction region, atmospheric pressure carrier gas (purified air), reactant gas (hexachloroethane), and an internal calibrant (4-nitrobenzotrile) are ionized by a ⁶³Ni 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, or 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 a plasmagram. The plasmagrams were analyzed automatically by the programmed algorithm in the instrument. In the analyses by IMS in this study, 2 µL of the solutions obtained from the extracted adhesive tapes (see below) were placed on the fiberglass 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.

SEM/EDX—CamScan III SEM and CamScan IV SEM were combined with Tracor-Northern 5400 and Tracor-Northern 5500 EDS systems, respectively.

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 (unless stated otherwise). The ventilation in the range was turned off during the experiments. Several individuals participated in shooting experiments. One round was fired. For sampling hands and hair of a shooter, 25 mm aluminum stubs coated with 12 mm diameter conductive double side adhesive tapes (Agar Scientific Ltd.) were used. Both hands of each shooter were sampled by the same stub, applying 25 dabs for each back area of a hand, starting with the right hand (13). Using an additional stub, the front half of the shooter's hair was sampled, applying 200 dabs (13). The sampling was carried out at different time intervals (5 min, 1 h, and 3 h) after firing. Between firing and sampling (except the 5 min interval), the subjects carried out their usual work in the laboratory (in an area not exposed to firearms discharge residues) Altogether, nine shooting experiments of one round were carried out.

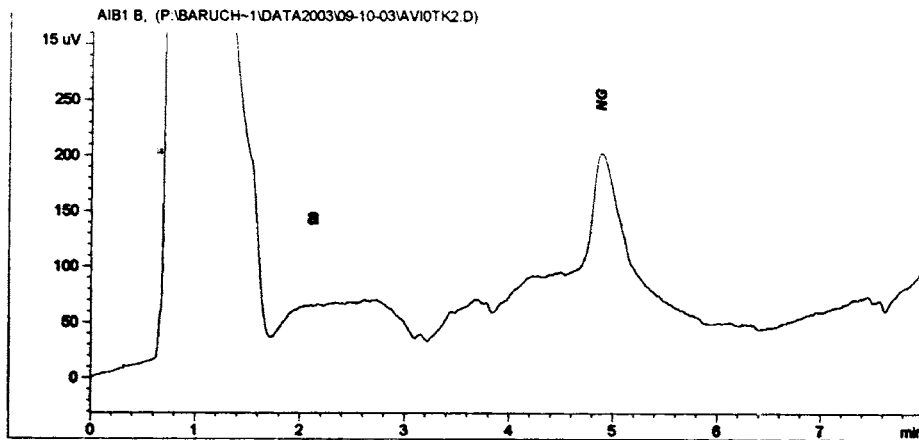
Extraction of Gunpowder Residues from Stubs and Their Analysis

Several solvents (acetone, methylene chloride, water, and water/ethanol mixtures) were examined for the extraction efficiency of the propellant constituents from the double-side adhesives.

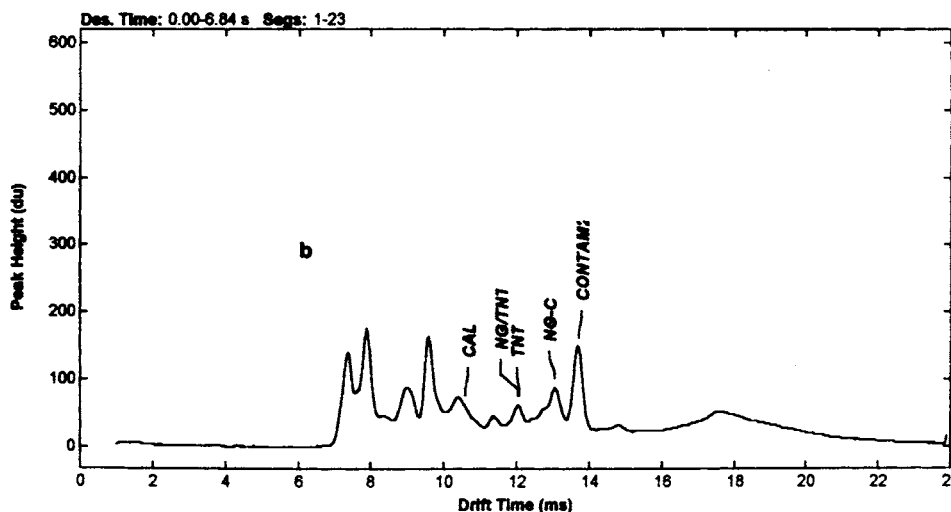
In the preliminary experiments using acetone or methylene chloride as solvents for extraction, several microliters of a standard working solution mixture of NG and DNT were placed on an adhesive coated stub and dried for about 2 min at room temperature. After the addition of a standard solution, some of the stubs were also used to dab the clean hands of an individual 50 times to examine the influence of the sampled skin debris on the extraction. The stub was put in a 25 mL glass beaker to which 15 mL of a solvent were added (a quantity sufficient to cover the stub), and the extraction was carried out at different times and at ambient or lower temperatures, with or without sonication. Lower than ambient temperatures, down to melting points of the solvents, were obtained by cooling with liquid nitrogen. When using an organic solvent for extraction, after the stub was removed from the beaker, the extract was evaporated to about 0.4 mL using a stream of dry nitrogen and transferred to a conical vial of 0.5 mL, where it was concentrated to about 20 µL. The obtained solution was analyzed by GC/TEA and IMS (2 µL for each instrument). The extraction efficiency was assessed using the results obtained by GC/TEA. To elucidate only the effect of extracted components from the adhesives and/or skin debris on the sensitivity of GC/TEA to NG and DNT, the extraction experiments were conducted as described above, except the step of depositing the standard solution on the stub. Only the concentrated extract was spiked with the standard solution prior to the analysis by GC/TEA.

Since it was found that extraction with the organic solvents results in high interference from the adhesives and skin debris, decreasing the sensitivity of GC/TEA to NG and DNT (in particular to NG), it was decided to focus on extraction experiments with water or water/ethanol mixtures (water, the major component) (9–11). The

² Chem Service Ltd., P.O. Box 599, West Chester, PA 19381.



BARRINGER IONSCAN Results (Explosives) ***** ALARM *****
 Sample: evi-0-80c-30-sony take-2 baruch 3991a File: AVI0TK2.EXP
 Context:



Des. Time: 0.00-6.84 s Segs: 1-23
 Time: 10:59:40 Date: Sep/10/2003 IONSCAN: Model: 400 - 11273 Des. Time: 6.84 s Segs: 23 Multi-stage: 3
 Temps: (°C): Drift Tube: 110 Inlet: 238 Desorber: 227 Flows (cc/min): Drift: 404 Sample: 214
 Path: C:\MSAMP\09_10_03\AVI0TK2.EXP
 Alarms: NG, TNT

Channel Summary:

Channel	DTime	Ko	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.589	1.6520	1.00000	722		+88	
CONTAM2	13.887	1.2771	1.00000	264	1750	-13	8
NG-C	13.058	1.3396	1.00000	96	897	-4	8
NG/TNT	12.051	1.4516	1.00000	106	343	+0	4
TNT	12.656	1.4510	1.00000	106	446	-6	7

FIG. 1—Analysis of the water extract (1 h extraction) of the hands' sample collected 5 min after firing (see text): (a) GC/TEA chromatogram of the methylene chloride concentrate, (b) Plasmagram of the concentrate.

solubility of NG and 2,4-DNT in water at 25°C is 1500 µg/mL and 270 µg/mL, respectively (10). To increase the stability of NG in water or water/ethanol mixtures, sodium azide was added to all of them, in a concentration of 0.1% w/v (concentration in water) (9), so that all the extraction experiments with water or water/ethanol mixtures contained sodium azide in water. In these experiments the extraction from a stub was carried out (as described above using organic solvents) with and without sonication at various temperatures

(from ambient up to 80°C, the maximum temperature attainable in the sonicator). The obtained extract was transferred from the beaker to a separation funnel to which 15 mL of methylene chloride were added. After extraction for 2 min, the lower phase of methylene chloride was transferred to a 25 mL glass beaker, and the procedure of concentration of the extract by evaporation was continued as described above for the extraction with organic solvents. No additional clean-up steps were employed. The extraction experiments with

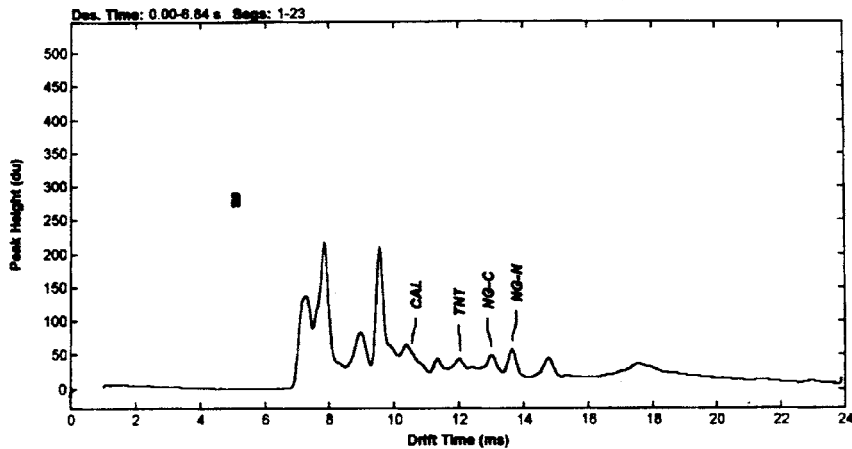


IONSCAN Results (Explosives)

*** ALARM ***

Sample: baruch-1h 30-sony80c take-1 baruch 4002a
Context:

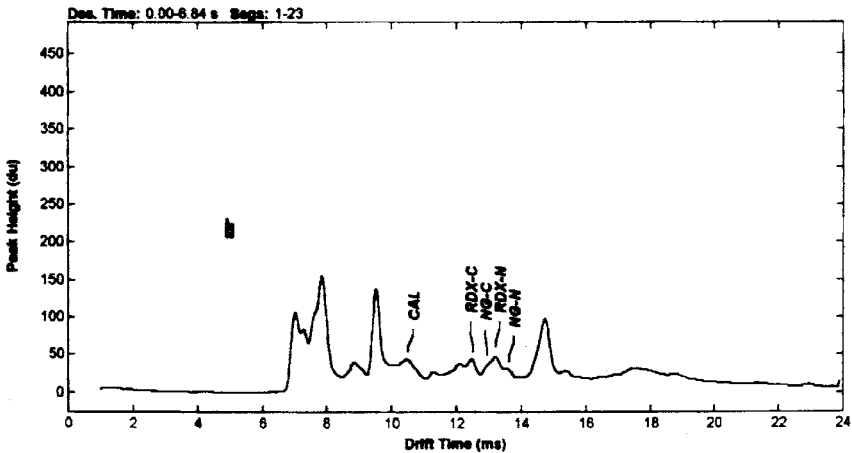
File: BARUC-1H.EXP



Time: 11:07:44 Date: Sep/10/2003 IONSCAN: Model: 400 - 11273 Des. Time: 6.64 s Segs: 23 Multi-stage: 3
Temps: (°C): Drift Tube: 109 Inlet: 239 Desorber: 227 Flows (cc/min): Drift: 404 Sample: 204
Path: C:\MSAMP\09_10_03\BARUC-1H.EXP
Alarms: NG

Channel Summary:

Channel	DTime	Ko	CF	Max Amt	Cum Amt	Delta	# Hits
CAL	10.567	1.6620	1.00000	647		+53	
NG-C	13.010	1.3396	1.00000	67	112	+8	2
NG-N	13.667	1.2742	1.00000	106	666	-33	10
TNT	12.810	1.4810	1.00000	47	156	+18	4



Time: 15:03:24 Date: Sep/10/2003 IONSCAN: Model: 400 - 11273 Des. Time: 6.64 s Segs: 23 Multi-stage: 3
Temps: (°C): Drift Tube: 109 Inlet: 239 Desorber: 227 Flows (cc/min): Drift: 404 Sample: 204
Path: C:\MSAMP\09_10_03\ARYE3H.EXP
Alarms: NG, RDX

Channel Summary:

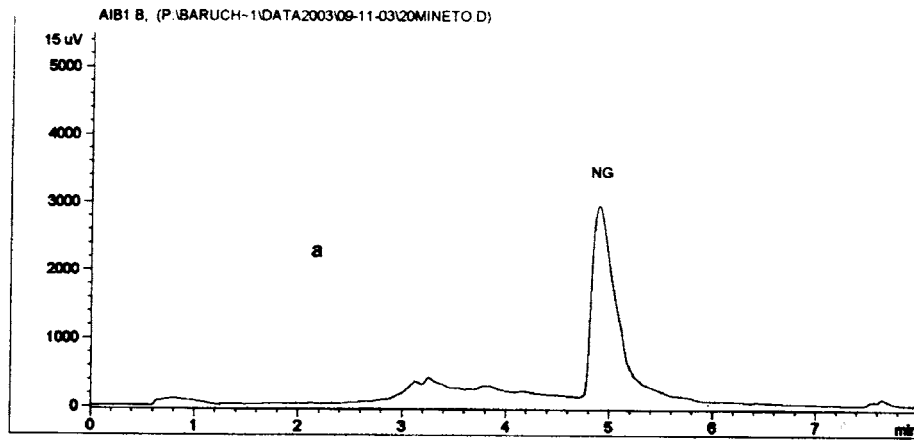
Channel	DTime	Ko	CF	Max Amt	Cum Amt	Delta	# Hits
CAL	10.518	1.6620	1.00000	222		+26	
NG-C	12.971	1.3396	1.00000	72	325	+8	5
NG-N	13.637	1.2742	1.00000	37	133	-32	4
RDX-C	12.512	1.3867	1.00000	38	210	-30	7
RDX-N	13.232	1.3132	1.00000	43	296	-2	8

FIG. 2—Plasmagrams of the methylene chloride concentrates of the water extracts (1 h extraction) of two hands' samples: (a) a sample collected 1 h after firing, (b) a sample collected 3 h after firing.

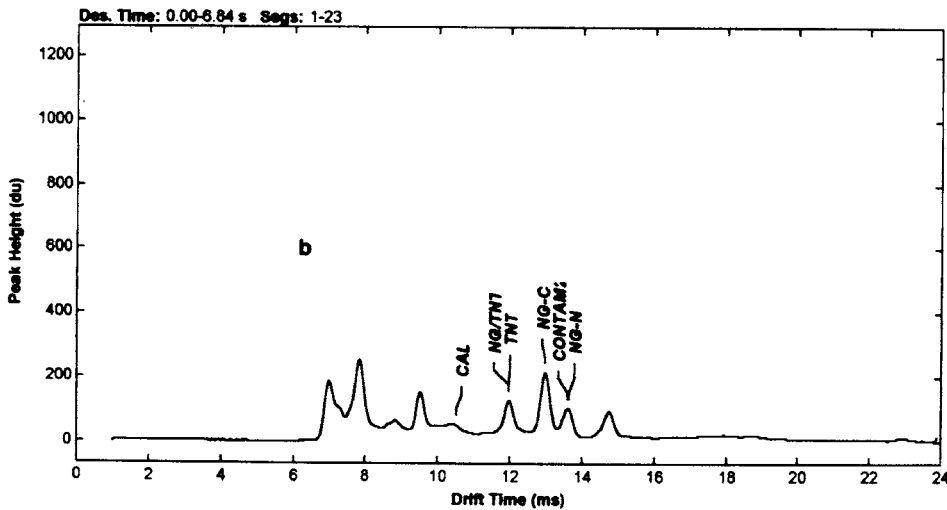
water and water/ethanol mixtures started with gunpowder residues and not with standard solutions of NG and DNT as follows:

First, a small (several tenths of one mm) particle from a spent Winchester ammunition cartridge was mounted on an adhesive

coated stub under a stereo-microscope. Following the mounting, the stub was used to dab both hands of one individual 50 times. After extraction with water, the particle was removed from the stub by tweezers and dissolved in methylene chloride. Using GC/TEA, the amount of NG recovered by water extraction was compared to



BARRINGER IONSCAN Results (Explosives) *** ALARM ***
 Sample: 20min etoh 10% mizuy baruch 4030a File: 20MINETO.EXP
 Context:



Time: 13:01:14 Date: Sep/11/2003 IONSCAN: Model: 400 - 11273 Des. Time: 6.84 s Segs: 23 Multi-stage: 3
 Temps: (°C): Drift Tube: 109 Inlet: 238 Desorber: 226 Flows (cc/min): Drift: 404 Sample: 196
 Path: C:\MSAMP\09_11_03\20MINETO.EXP
 Alarms: NG

Channel Summary:

Channel	DTime	Ko	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.515	1.6520	1.00000	407		+23	
CONTAM2	13.802	1.2771	1.00000	226	998	+23	5
NG-C	12.967	1.3396	1.00000	560	3665	+14	11
NG-N	13.633	1.2742	1.00000	228	1368	-11	9
NG/TNT	11.967	1.4516	1.00000	339	1812	+10	8
TNT	11.972	1.4510	1.00000	338	1828	+5	9

FIG. 3—Analysis of the water/ethanol (10% ethanol) extract (20 min extraction) of the hands' sample collected 5 min after firing: (a) GC/TEA chromatogram of the methylene chloride concentrate, (b) Plasmagram of the concentrate.

the amount of NG left in the particle and dissolved by methylene chloride.

The extraction efficiency experiments for NG were also carried out on samples collected from the hands of a shooter immediately (5 min) after shooting. Water and water/ethanol mixtures (10% v/v and 20% v/v ethanol) were used at 80°C with sonication. Ethanol was added to reduce the extraction time. In these experiments, extraction of the same stub was carried out three times consec-

utively (30 min each time for water extraction, up to 90 min total time and 10 min each time for water/ethanol extraction, up to 30 min total time). Each extract was analyzed by the GC/TEA and the IMS to evaluate the effect of extraction time on the recovery of NG. Based on the obtained results, the optimal procedure for extraction was assessed. This procedure was examined for extraction of the standard working solutions of NG and DNT, as well as for single gunpowder particles from the adhesive

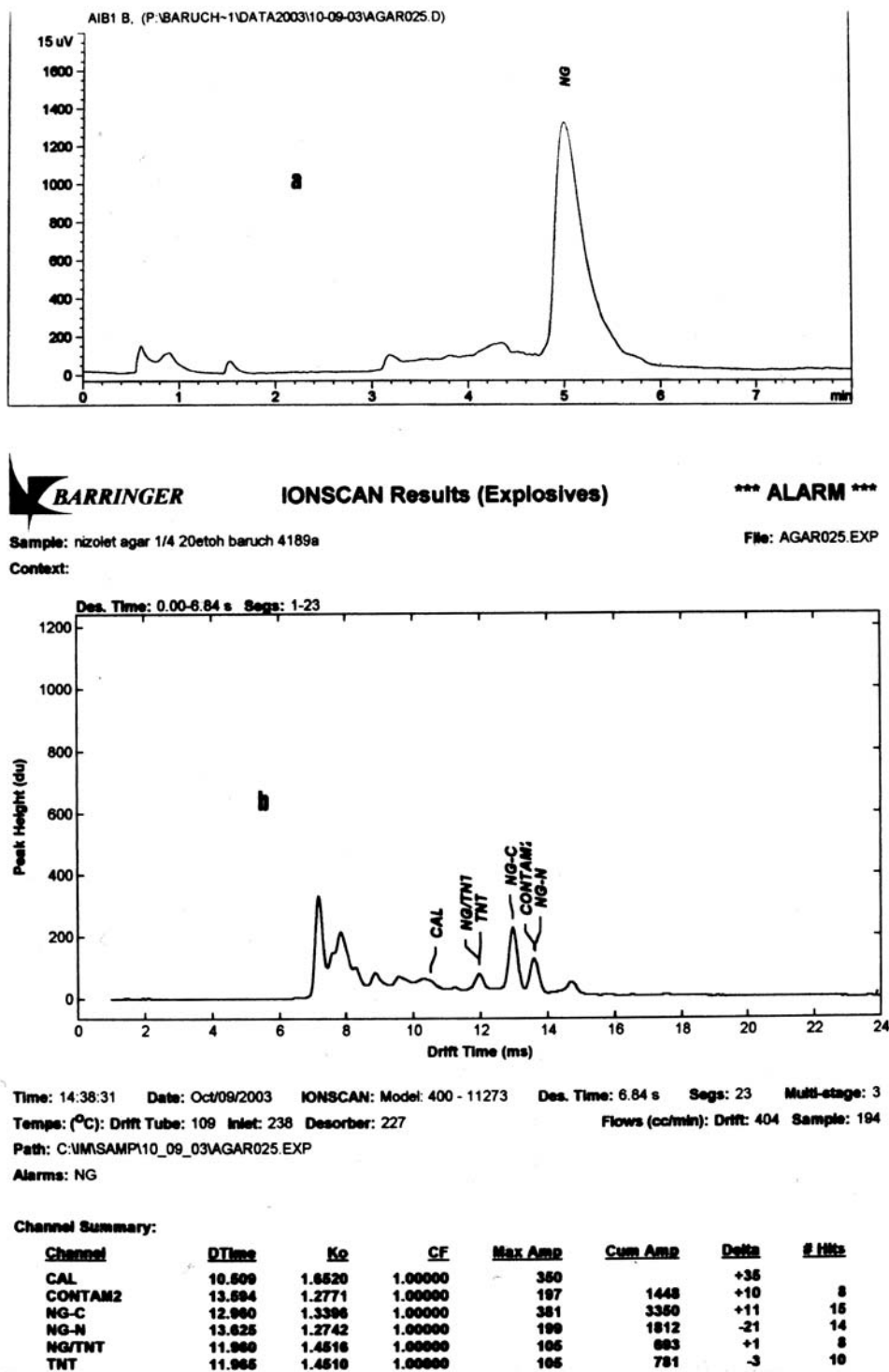


FIG. 4—Analysis of the water/ethanol (20% ethanol) extract (for optimal procedure see text) of the standard solution of NG; dabbing of hands: (a) GC/TEA chromatogram of the methylene chloride concentrate, (b) Plasmagram of the concentrate.

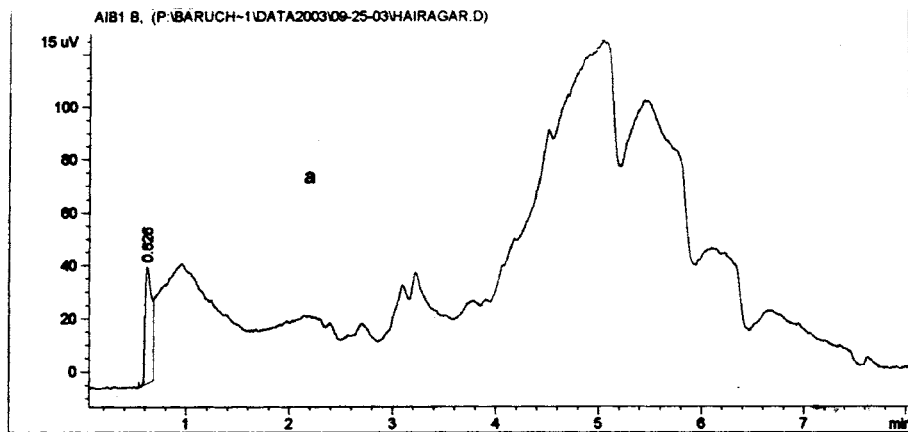
coated stubs. The procedure was also tested in shooting experiments.

Results and Discussion

The approximate limits of detection (LOD) of the GC/TEA and the IMS employed in this study for NG and DNT were reported previously (7) and are in the range of 0.1–1 ng. The composition of gunpowder in the Winchester ammunition used in this research

(as analyzed by GC/MS) was as follows (7): 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 nitrocellulose (NC), which could not be analyzed by GC/MS.

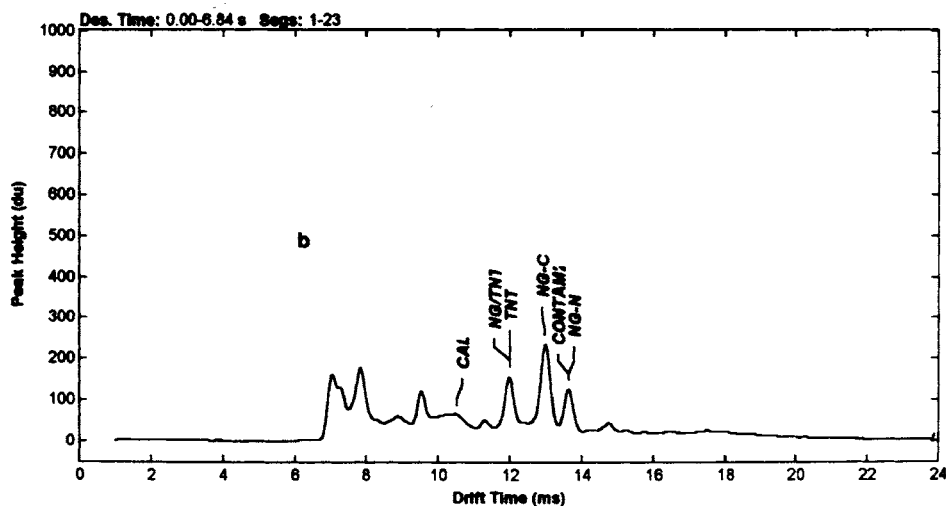
Extraction experiments carried out with acetone and methylene chloride resulted in co-extraction of adhesive and skin components that interfered considerably in the analysis of NG and DNT by GC/TEA and degraded its sensitivity. The interferences were


IONSCAN Results (Explosives)
***** ALARM *****

Sample: hair agar st100 20%eto baruch 4092a

File: HAIRAGAR EXP

Context:



Time: 12:10:53 Date: Sep/25/2003 IONSCAN: Model: 400 - 11273 Des. Time: 8.84 s Segs: 23 Multi-stage: 3
 Temps: (°C): Drift Tube: 109 Inlet: 238 Desorber: 227 Flows (cc/min): Drift: 404 Sample: 178
 Path: C:\MSAMP\09_25_03\HAIRAGAR.EXP
 Alarms: NG

Channel Summary:

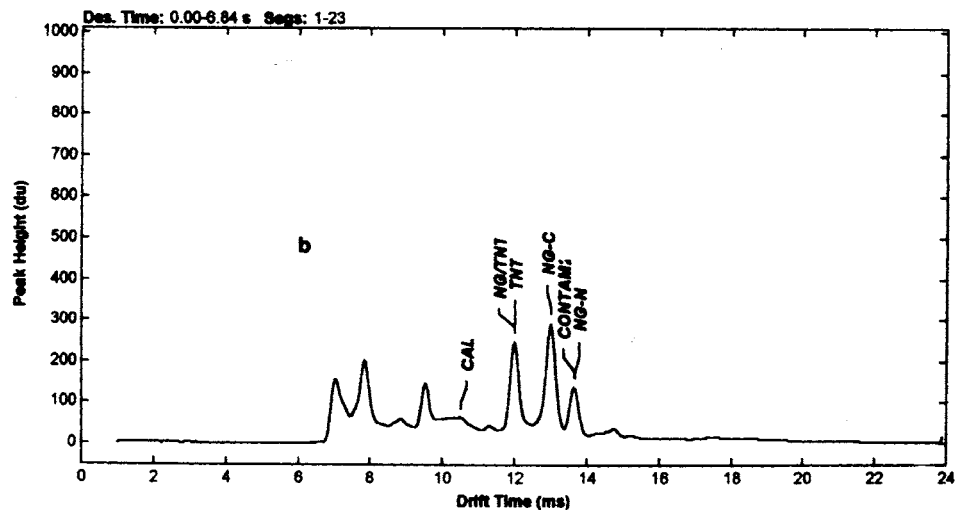
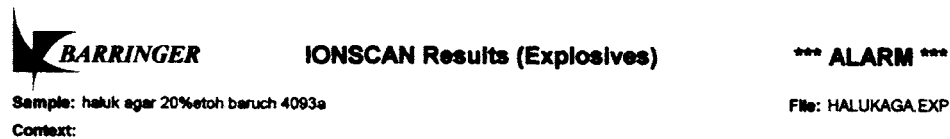
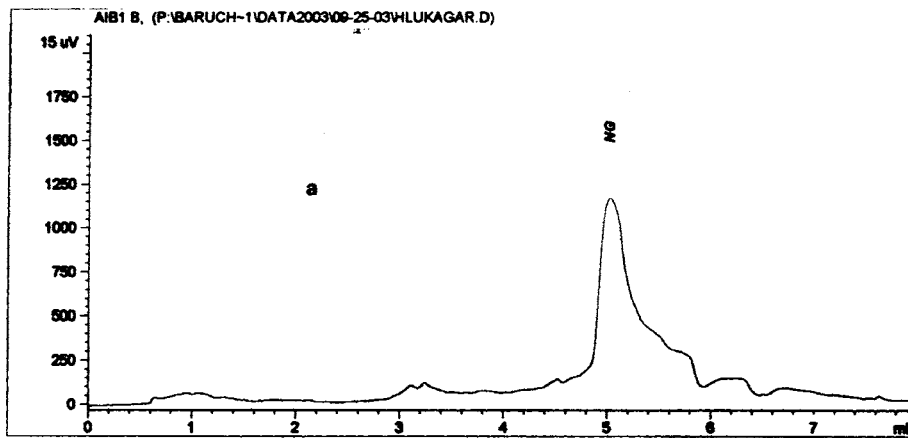
Channel	DTime	Ke	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.629	1.6620	1.00000	523		+39	
CONTAM2	13.629	1.2771	1.00000	220	1371	+21	7
NG-C	12.984	1.3388	1.00000	526	3641	+8	11
NG-N	13.851	1.2742	1.00000	221	1738	-13	12
NG/TNT	11.983	1.4516	1.00000	317	2053	+4	10
TNT	11.988	1.4518	1.00000	317	2139	+0	12

FIG. 5—Same as Fig. 4, but dabbing of hair.

observed even when the extractions were conducted at very low temperatures (close to melting point of the solvents) and for relatively short periods of time (several minutes).

As was described in the previous paragraph, based on previous studies (9–11), it was decided to experiment with water (containing 0.1% w/v of sodium azide) and water/ethanol mixtures (water, the major component) to find the best conditions for maximizing the recovery of NG from gunpowder residues mounted on stubs and keeping the co-extraction of interfering substances from the

adhesives and skin to a minimum. It was found that conditions of high temperatures with relatively long periods of sonication are necessary for extraction with water to obtain considerable recovery of NG. Thus, only about 10% recovery of NG were obtained from a single gunpowder residue particle mounted on a stub and extracted for 30 min at 80°C with sonication. It should be reiterated that the stubs with mounted particles were used to dab the hands of a person 50 times prior to extraction. No significant sensitivity degradation of the GC/TEA for NG was observed.



Time: 12:23:28 Date: Sep/25/2003 IONSCAN: Model: 400 - 11273 Des. Time: 6.84 s Segs: 23 Multi-stage: 3
 Temps: (°C): Drift Tube: 109 Inlet: 238 Desorber: 227 Flows (cc/min): Drift: 402 Sample: 176
 Path: C:\MSAMP\09_25_03\HALUKAGA.EXP
 Alarms: NG

Channel Summary:

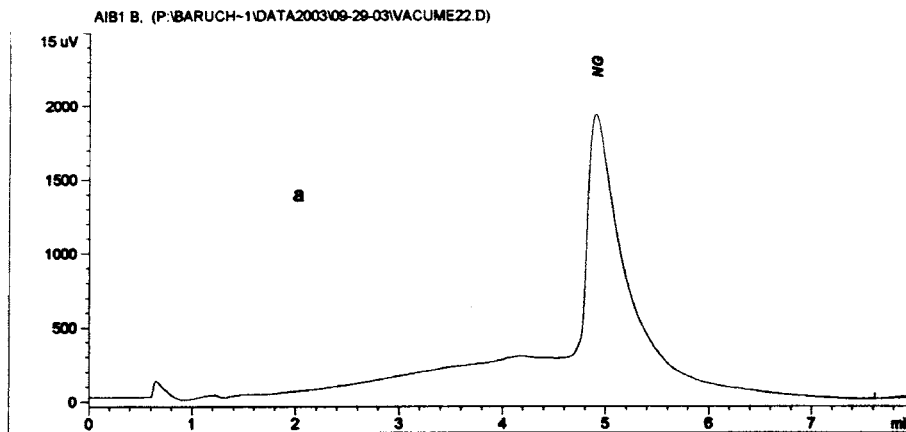
Channel	DriftTime	Ko	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.832	1.6620	1.00000	578		+44	
CONTAM2	13.624	1.2771	1.00000	199	1305	+22	7
NG-C	12.968	1.3396	1.00000	814	4626	+8	14
NG-N	13.666	1.2742	1.00000	291	1926	-13	14
NG/TNT	11.996	1.4616	1.00000	489	3478	+7	12
TNT	11.991	1.4616	1.00000	489	3509	+2	13

FIG. 6—Same as Fig. 4, but dabbing of a cotton cloth.

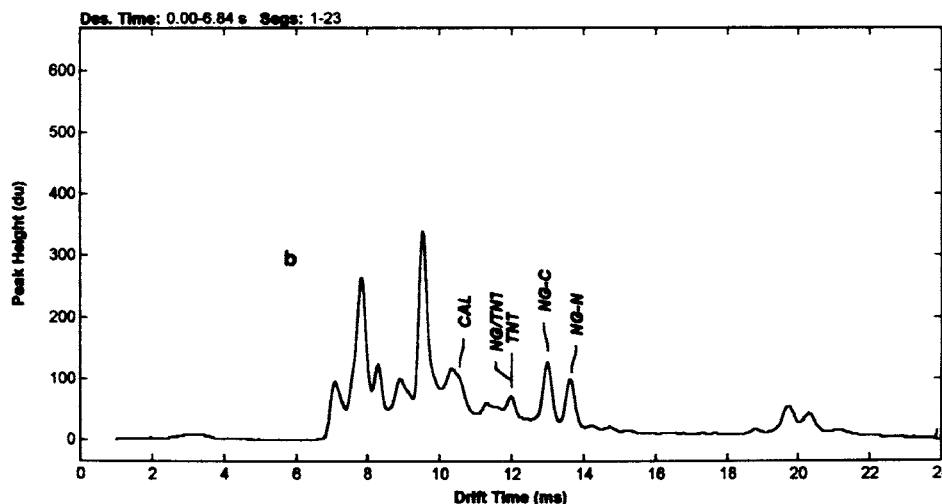
When a stub with a mounted gunpowder particle on the non-conductive double side adhesive was coated with carbon (for SEM/EDX examination), the extraction efficiency decreased tremendously, so that NG could not be detected by GC/TEA. However, when using conductive adhesives, there is no need to coat samples for high vacuum SEM/EDX examination. Nonconductive samples may be examined without conductive coating in a low vacuum, using variable pressure or environmental SEM. Since the two SEMs used in the study are of a high vacuum type, the shooters'

hands and hair in the shooting tests were sampled with conductive (Agar Scientific Ltd.) double side adhesive coated stubs.

It was found that when using water as a solvent for extraction, approximately 1 h of sonication at 80°C is necessary to attain most of the NG recovery from propellant residues sampled by a stub from the hands of a shooter (Fig. 1). The figure shows positive results for NG in both instruments, the GC/TEA and the IMS for the sample collected immediately (5 min) after shooting. As was explained previously (7), detection of at least two peaks of NG



BARRINGER IONSCAN Results (Explosives) *** ALARM ***
 Sample: vacume overnight stab3 baruch 4107a File: VACUM2.EXP
 Context:



Des. Time: 0.00-6.84 s Segs: 1-23
 Time: 10:19:34 Date: Sep/30/2003 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: 192
 Path: C:\MSAMP\09_30_03\VACUM2.EXP
 Alarms: NG

Channel Summary:

Channel	DTime	Ka	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.537	1.6620	1.00000	841		+42	
NG-C	12.994	1.3396	1.00000	219	2320	+1	19
NG-N	13.861	1.2742	1.00000	143	1781	-28	19
NG/TNT	11.862	1.4616	1.00000	96	426	-2	6
TNT	11.997	1.4616	1.00000	96	888	-13	19

FIG. 7—Same as Fig. 4, but the extract of the hands' sample taken 5 min after firing. The stub was held 17 h in the SEM prior to the extraction.

(out of the possible three) in a plasmagram is marked by IMS as “Alarm”. Figure 1b shows that two peaks of NG were detected by the IMS. DNT was not detected in the collected sample, because its concentration in the gunpowder of the tested ammunition was much lower than NG (7). After an additional 30 min of extraction from the same sample, no NG was detected in the IMS or in the GC/TEA. Figure 2 shows positive results for NG in the IMS for the hands' samples collected one and three hours after firing. In Fig. 2a a labeled peak for TNT is shown in the plasmagram. Since the drift times of the TNT peak and one of the NG peaks are very close, the

instrument almost always labels such a peak as NG and TNT (see Figs. 1b, 3–8b, and 9). In such cases when there is “alarm” for NG, the presence of TNT is questionable and as may be seen the system did not “alarm” for TNT in Fig. 2a. Figure 2b shows “alarm” for NG and RDX (two peaks). A possible explanation for the presence of RDX in the above sample may be contamination. The samples shown in Fig. 2 were negative for NG in the GC/TEA. The samples from front hair of three shooters collected 5 min, 1 h, and 3 h after firing and extracted by water were negative for NG in both instruments. A possible explanation for this result may be that

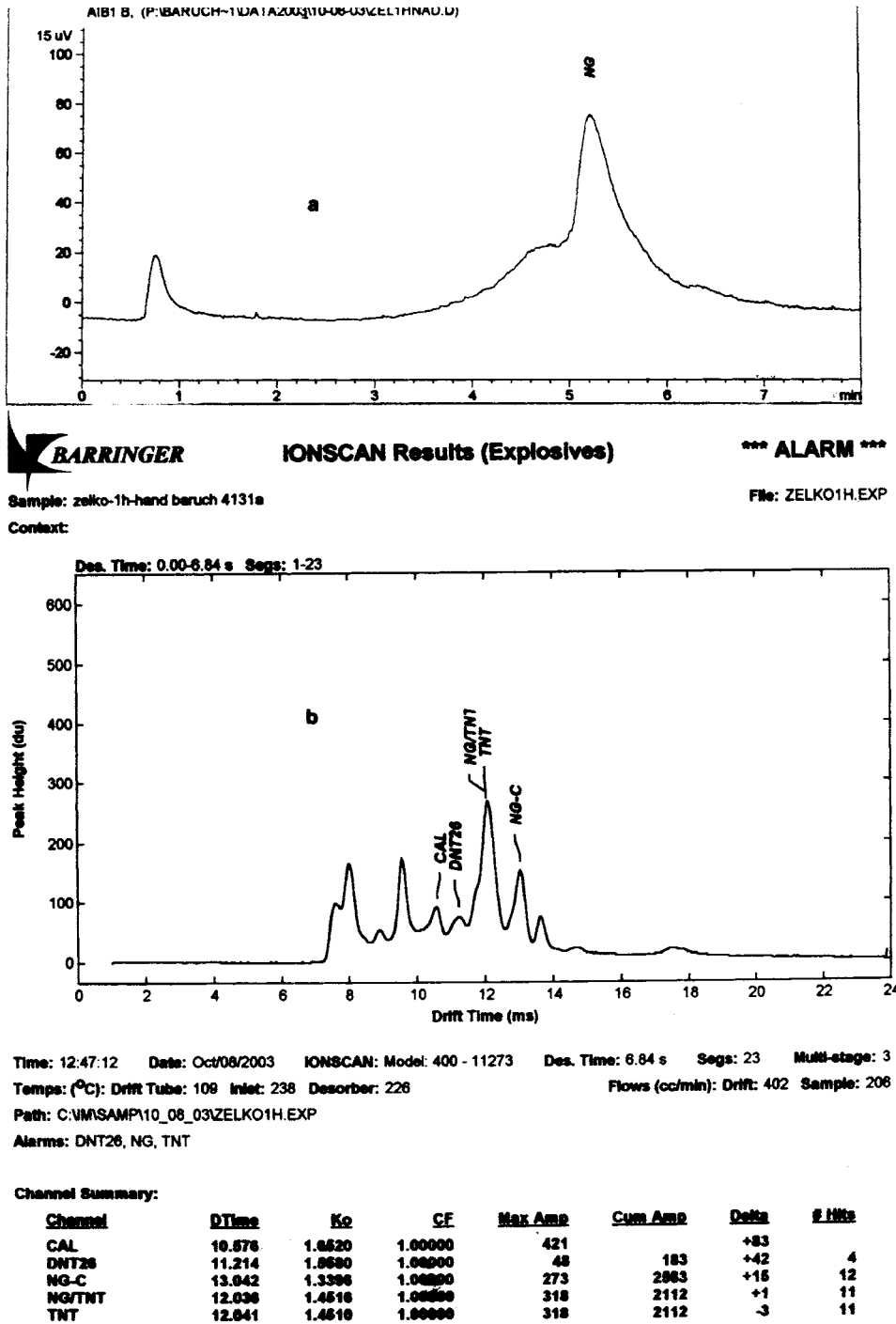


FIG. 8—Same as Fig. 7, but the extract of the hands' sample taken 1 h after firing.

much smaller amounts of gunpowder residues reach the head of a shooter than those deposited on his hands. Possible interferences in the analysis of samples collected from hair are discussed below.

Since one hour for extraction is quite a long time from an operational point of view, experiments were carried out with water/ethanol mixtures to reduce the extraction times. It was found that when using water/ethanol mixture (10% ethanol), most of the NG recovery occurs after 20 min of extraction (Fig. 3). An additional 10 min of extraction using this solvent provided a positive result for NG only in the IMS and not in the GC/TEA. When using a water/ethanol mixture (20% ethanol), most of the NG recovery

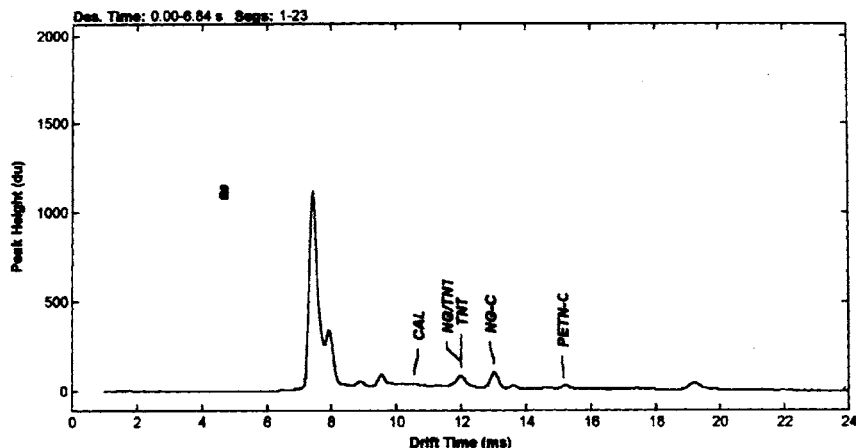
occurred after 10 min of extraction (positive results for NG in both instruments). Two additional extractions (for 10 min) of the same sample resulted in detection of NG only in the IMS. The results show that the addition of ethanol to water, even in relatively low concentrations, reduces the extraction time very considerably.

It is interesting to note that IMS appears to be a more sensitive method for NG than GC/TEA, regarding the samples obtained by water or water/ethanol extraction. As could be seen, several samples (see also below) negative for NG in the GC/TEA were positive for NG in the IMS (at least two peaks in a plasmagram). The opposite has not been observed in this study. This phenomenon has not been

BARRINGER IONSCAN Results (Explosives) *** ALARM ***

Sample: arye hand 3h baruch 4171a
Context:

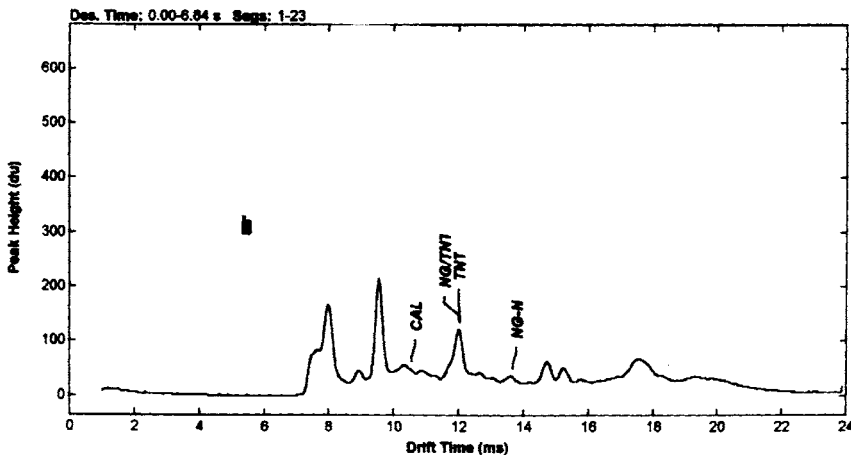
File: ARYEHAND.EXF



Time: 15:04:03 Date: Oct/08/2003 IONSCAN: Model: 400 - 11273 Des. Time: 6.84 s Segs: 23 Multi-stage: 3
Temp: (°C): Drift Tube: 109 Inlet: 239 Desorber: 227 Flows (cc/min): Drift: 404 Sample: 206
Path: C:\MSAMP\10_08_03\ARYEHAND.EXP
Alarms: NG, TNT

Channel Summary:

Channel	DTime	Ko	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.861	1.8620	1.00000	358		+85	
NG-C	13.012	1.3396	1.00000	371	1219	+9	5
NG/TNT	12.008	1.4516	1.00000	317	806	-10	4
PETN-C	16.187	1.1462	1.00000	33	120	+30	4
TNT	12.813	1.4516	1.00000	317		-16	5



Time: 14:07:09 Date: Oct/08/2003 IONSCAN: Model: 400 - 11273 Des. Time: 6.84 s Segs: 23 Multi-stage: 3
Temp: (°C): Drift Tube: 109 Inlet: 239 Desorber: 227 Flows (cc/min): Drift: 402 Sample: 206
Path: C:\MSAMP\10_08_03\ARYE3HHA.EXP
Alarms: NG, TNT

Channel Summary:

Channel	DTime	Ko	CF	Max Amp	Cum Amp	Delta	# Hits
CAL	10.868	1.8620	1.00000	428		+71	
NG-N	13.988	1.2742	1.00000	34	226	-24	7
NG/TNT	12.818	1.4516	1.00000	518	3160	-4	9
TNT	12.821	1.4516	1.00000	518	3225	-8	11

FIG. 9—Plasmagrams of the methylene chloride concentrates using the optimal procedure, (a) a sample collected from hands 3 h after firing, (b) a sample collected from hair 3 h after firing.

observed in the previous study on vacuum collected samples from clothing, which were extracted by methylene chloride (7). At this stage we do not have any plausible explanation for this difference.

Based on the extraction efficiency results reported above, it was decided that the optimal procedure for extraction will use a water/

ethanol mixture (20% ethanol) at 80°C with sonication for 15 min. It should be pointed out that sonication is imperative for efficient extraction. It was found that just occasional stirring of the stub in the beaker greatly reduces the extraction efficiency. It is important to note that methylene chloride extracts a small amount of water

from the water/ethanol mixtures. The presence of ethanol probably facilitates this phenomenon. Water separates from the organic phase during concentration of the methylene chloride phase by evaporation and is discarded from the extract after the concentrate is transferred from the beaker to a conical vial.

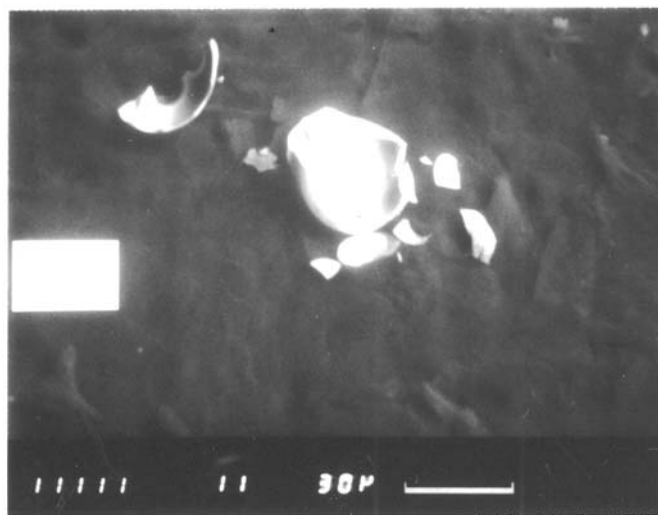
The optimal procedure was tested in extraction experiments of single gunpowder particles and of standard solutions of NG and 2,4-DNT deposited on stubs, as well as in additional shooting tests. The obtained recovery of NG and DNT was quite variable and found to be in the range of 30–90% for the three tested adhesives, which were used to dab hands 50 times after the deposit of standard solutions or after mounting of a single gunpowder particle. Coating of the stubs with carbon reduced the extraction efficiency tremendously. The recovery from Agar adhesive, the only adhesive used in the shooting tests, was also examined after dabbing hair 200 times and cotton cloth 50 times. Figures 4–6 show the obtained results. Figure 5a shows that hair interferes tremendously in the GC/TEA analysis, preventing detection of NG by this method. No interference was observed for the same sample in the IMS (Fig. 5b). The hair interference in the GC/TEA cannot account for the negative results in the samples collected from the shooters' hair, since those samples were also negative in the IMS. No interferences were observed from skin or cotton fibers in the GC/TEA (Figs. 4 and 6).

Figures 7–9 show the results of the extracted samples from hands (by the optimal procedure) in the shooting tests. It may be seen that positive results in the GC/TEA and in the IMS were obtained for 5 min and 1 h samples. The 5 min sample was kept 17 h in the SEM prior to extraction. The obtained positive result for NG indicates that a high vacuum in the SEM does not cause a significant evaporation of NG from propellant residues. The 3 h sample was positive in the IMS (two peaks in plasmagram) only. Again, the 5 min and 1 h samples from hair of the shooters were negative for NG in both instruments. Surprisingly, the 3 h sample was positive in IMS (two peaks). A possible explanation for this result may be contamination of the hair by the hands of the shooter.

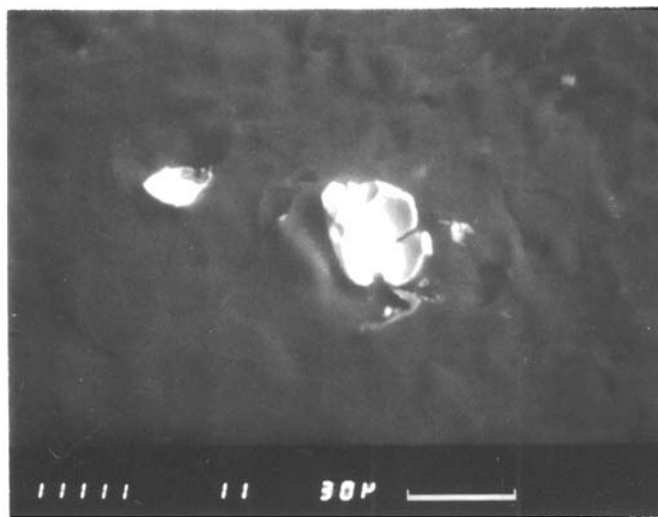
The amounts of NG recovered from the shooters' hands immediately after firing could be estimated from the obtained GC/TEA chromatograms in comparison to the chromatograms of the standard solutions. The quantities were highly variable, in the range of 20–200 ng, and in general, comparable to the amounts reported for hands-swabs in the previous studies (14–16).

It was of interest to see what happens to primer (GSR) residues on an adhesive after the extraction procedure. For this purpose, a 5 min sample was examined with a SEM prior to extraction. Two random clusters of relatively large GSR particles at different locations on the stub were photographed, and their coordinates on the stub were documented. After extraction and drying, the stub was examined again in the SEM. It was observed that not all GSR particles in one location were dislodged from the adhesive during the extraction (Fig. 10). In the second examined location on the stub, all the photographed GSR disappeared after the extraction.

Since the present operational method for sampling GSR implemented by the Israel Police uses nonconductive double side adhesive, the developed method has not been experimented so far in casework. We are planning to conduct a pilot study in casework by changing the nonconductive double side adhesive to conductive ones in a number of sampling kits for GSR used by the Israeli scene of crime officers. The samples obtained with these kits will be analyzed for GSR by SEM/EDX, followed by the new method for gunpowder residues analysis. Laboratories that have at their disposal either variable pressure or environmental SEM should be able to use nonconductive double-side adhesives without carbon coating for GSR analysis.



a



b

FIG. 10—Backscattered SEM micrographs of the GSR particles (see text): (a) before extraction, (b) after extraction.

The analytical methods used in this study were GC/TEA and IMS, the only methods available to us that are sensitive for real life samples (GC/MS is not sensitive enough (7)). Other reported appropriate methods are HPLC/PMDE (4,15) and GC/IMS (17).

Conclusion

Results of the present study show that it is feasible to extract and analyze propellant residues from double-side adhesive coated stubs used for sampling suspects for GSR. The optimal procedure for extraction employs water/ethanol (80/20) mixture at 80°C with sonication for 15 min. The residues from the obtained extract are further extracted with methylene chloride and concentrated by evaporation for analysis by GC/TEA and IMS. The extraction may be carried out after the analysis of the samples for primer GSR by SEM/EDX. When using a high vacuum SEM it is imperative to use conductive double-side adhesives for sampling to avoid carbon coating, which impairs tremendously the extraction efficiency.

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