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Systematic Analysis of Explosive Residues

Examination of bomb scene evidence is an area of increasing involvement for the forensic scientist in which incidents may vary from student mischief to mass murder. To undertake explosive casework responsibilities, the scientist must have personal experience of the type of physical evidence left after explosions, including device remains, characteristic damage, and chemical residues.

Recognition of device remains is aided by law enforcement agency publications [1-6]. Explosive damage to metal has been studied [7] and the significance of damage in bomb incident investigations has been discussed in general terms [8]. Chemical residues may contain unreacted explosive components [9-13] and also condensed reaction products [12,14]. Solid products have been studied less than gaseous products, but have been reviewed for black powder [14,15] and chlorate and perchlorate mixtures [16]. Smokeless powders yield nitrites which form the basis of propellant powder pattern tests [17,18]. Since solid reaction products from dynamite do no work, their chemical composition has been deduced more from thermodynamic calculations than analysis [12,19].

Published methods for explosive residue analysis include microscopic examination for unreacted explosive [10,11], chemical spot tests [10,13,15,20,21], thin-layer chromatography (TLC) [9,10,22,23], and infrared spectroscopy [24,25].

This study presents a scheme for systematic analysis of explosive residues isolated by physical removal or solvent extraction. The techniques are a combination of infrared spectroscopy, TLC, X-ray diffraction, emission spectrography, microscopy, and chemical spot tests. Application to residue analysis is demonstrated by test explosions using black powder, single- and double-base smokeless powder, chlorate/sugar, dynamite, C4 plastic explosive, and PETN-based detonating cord (a glossary of terms is given in Appendix A).

Experimental

Analysis

The analytical scheme in Fig. 1 was applied to all of the explosives and their residues. Figures 2 and 3 expand on the solvent extracts.

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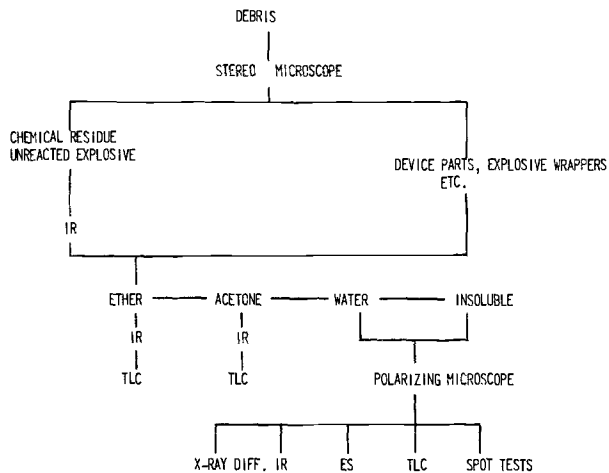


FIG. 1—General scheme for analysis of explosive residues.

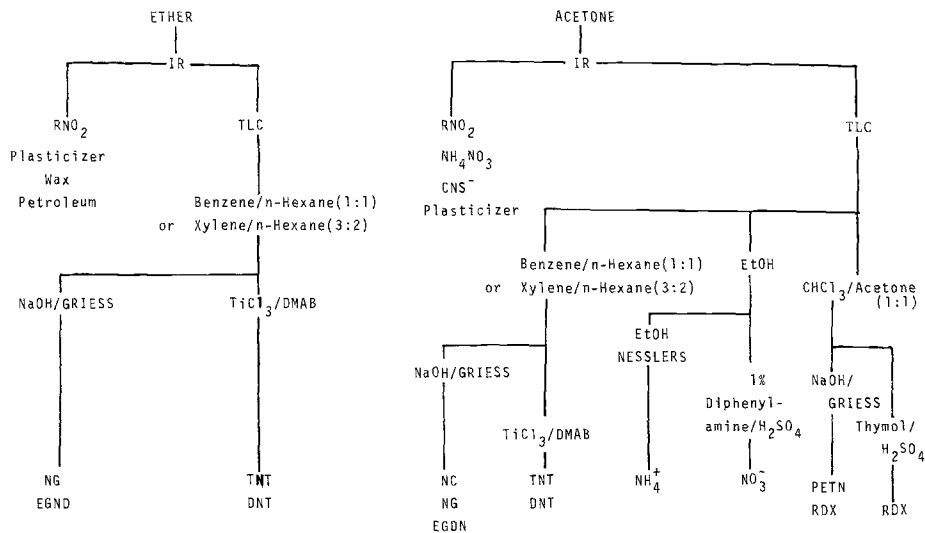


FIG. 2—Analysis of organic extracts.

Explosives and Explosions

Table 1 summarizes the explosives and conditions used in this study. Charges were made up and initiated by Explosive Ordnance Disposal (EOD) trained personnel using safety fuse, nonelectric blasting caps, and detonating cord boosters as required. Low explosives were confined in 1/8-in. wall steel pipes with threaded end caps. Explosive residue recovery procedures were concentrated on recognizable device remains, the crater, and adjacent surfaces.

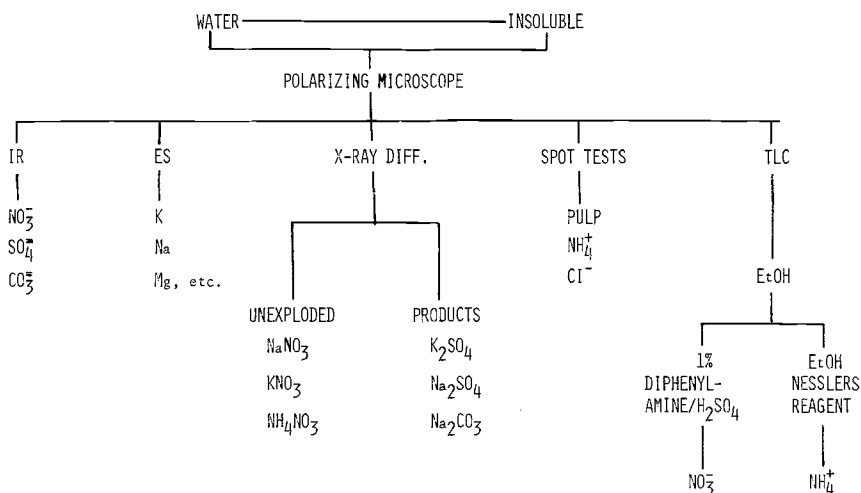


FIG. 3—Analysis of aqueous extracts.

Techniques

Infrared Spectroscopy—A Perkin Elmer Model 457A infrared spectrophotometer was used. Ether and acetone liquid extracts were sandwiched between 13-mm KBr disks and recovered by washing. Solids were analyzed as KBr pellets or nondestructively on a diamond cell (High Pressure Diamond Optics, McLean, Va.).

Infrared (IR) analysis may identify explosive components [24,25], inorganic ions [26], and contaminants, and may aid TLC selection and interpretation.

Thin-Layer Chromatography—TLC was run on 0.25-mm, precoated silica gel G glass plates (Mackery-Nagel and Co., Duren, Germany). Principal solvent systems were benzene [23], benzene/hexane [10], xylene/hexane [10], ethanol [9], and chloroform/acetone [9]. Developers were NaOH/Griess reagent [23], titanium trichloride/dimethylaminobenzaldehyde (TiCl₃/DMAB) [9], diphenylamine/H₂SO₄, and ethanol/Nessler reagent. The developers are applied as follows.

NaOH/Griess: Spray with 1N NaOH, hold in oven at 100°C for 10 min, cool, and spray with Griess reagent (0.25% sulfanilic acid and 0.1% α-naphthylamine in 1:1 aqueous acetic acid). Red spot for EGDN, NG, NC, RDX, PETN. High concentrations appear as a yellow spot with red edges [9]. TNT gives brown spots.

TiCl₃/DMAB: Spray with 15% TiCl₃/HCl, air-dry, and spray with DMAB reagent (1 g DMAB in 30 ml EtOH, 3 ml HCl 1:19, 180 ml BuOH). TNT and DNT give yellow spots [9].

Ph₂NH/H₂SO₄: Spray with 1% Ph₂NH in conc. H₂SO₄. Blue spot for nitrates.

EtOH/Nessler: Spray with EtOH followed by Nessler reagent. Orange spot for NH₄⁺.

X-Ray Powder Diffraction—Equipment was a Philips X-ray generator (PW 1130/00/60) with a copper diffraction tube (Type RD 60/2 PW 2103/00), operated at 50 mA, 40 kV, with 10 to 25-min exposure. A nickel filter removed Cu Kβ radiation. Samples were contained in 0.3-mm capillaries in Debye Scherrer 114.8-mm powder cameras. Ilford Industrial Type G X-ray film was used.

TABLE 1—Explosives and conditions.

Explosive	Source	Confinement	Surface
Black powder	Curtis-Harvey	pipe	sandbagged bunker, soil, 9 by 12-ft room
Smokeless, single base	Du Pont	pipe	sandbagged bunker, 9 by 12-ft room
Smokeless, double base	Hercules	pipe	sandbagged bunker, 9 by 12-ft room
Chlorate/sugar	homemade	pipe	sandbagged bunker
20% Polar [®] stumping powder (ammonia dynamite)	Canadian Industries Ltd.	unconfined	steel, wood
40% Forcite [®] (ammonia-gelatin dynamite)	Canadian Industries Ltd.	box pipe unconfined	sandbagged bunker sandbagged bunker, 9 by 12-ft room sponge rubber, carpet, clothing, ceiling tile, wood, 9 by 12-ft room
60% Forcite [®]	Canadian Industries Ltd.	unconfined	wood, gypsum wallboard, plastic base molding
75% Forcite [®]	Canadian Industries Ltd.	unconfined	steel
60% Geogel [®] (gelatin dynamite)	Canadian Industries Ltd.	unconfined	steel
C4 plastic explosive	Canadian Armed Forces	unconfined	steel, wood, sandbagged bunker
PETN detonating cord	Canadian Armed Forces	unconfined	aluminum, steel, wood, soil

X-ray powder diffraction permits nondestructive identification of crystalline materials by comparison to standards or by use of the American Society for Testing and Materials (ASTM) Powder Diffraction File [27].

Emission Spectrograph—Equipment was a Jarrell-Ash 3.4-m Ebert with dc arc excitation at 10 A for 10 s using a 10- μm slit. Samples were contained in $\frac{1}{8}$ -in. outside diameter carbon cups. The emission spectrograph was employed to identify explosive metallic content such as alkali metals, mineral contaminants such as boron in Chile saltpeter, and manufacturer additives.

Polarizing Microscope—Equipment was a Leitz Orthoplan[®] microscope equipped with an interference wedge (Leitz S-100) and a Mettler FP5-FP52 hot stage. This instrument permits nondestructive classification of crystalline materials by morphological analysis [28] and ready identification of isotropic substances by the Becke line technique for refractive index n_D .

Spot Tests—Spot tests were mainly those described by Amas and Yallop [13,20]. Chemical spot tests were used to check components such as NO_2^- , which in low yield (<10%) might be missed by instrumental analysis, and for rapid screening of a high yield of residue.

Results

Tables 2, 3, and 4 summarize the analysis of residues from the explosives listed in Table 1, by use of the scheme in Fig. 1.

Discussion

Low Explosives

Low explosives confined in steel pipes with threaded end caps exploded on flame initiation. Figure 4 illustrates damage to two series of pipes by charges of black powder, single-base smokeless powder (rifle propellant), double-base smokeless powder (pistol propellant), and (for comparison) dynamite. Fragmentation by chlorate/sugar was similar to single-base powder. The degree of fragmentation is seen to be much higher for double-base powder than for the other low explosives.

Table 2 summarizes the analysis of the low explosives and their residues using the scheme in Fig. 1.

Black powder gave pipe fragments with fresh rusty areas and a high yield of grayish residue. Unreacted granules were commonly recovered in pipe threads and sometimes in the body of the pipe. The surroundings were usually blackened. Figure 5 shows the effect of a 0.75-lb charge in a corner of a 9 by 12-ft room. Pipe fragments are shown in the bottom row of Fig. 4. Analysis of debris from this explosion is summarized in Table 2, No. 4. Thiocyanate was identified by IR spectroscopy in an acetone extract.

Black powder residue consisted primarily of potassium sulfate identified by X-ray powder diffraction. An IR spectrum of typical residue (Fig. 6) showed strong sulfate and weak nitrate. Weak carbonate peaks and absence of nitrate peaks were also observed in different explosions; that is, composition and distribution of explosive residue was not uniform. Reviews [14,15] suggest a higher percentage of potassium carbonate, but since it was not observed in X-ray powder diffraction patterns, this indicates that its yield is less than 10%. The safety fuse also gave potassium sulfate as principal residue from the black powder core.

The value of product identification is illustrated in Table 2, No. 3, since if the few

TABLE 2—Analysis of low explosive residues.

Number	Explosive	Residue-Bearing Surface	Microscopic Appearance	Components Identified
1	black powder		black granules	KNO ₃ , S, C
2	black powder	pipe and soil	gray crystalline black deposit	NO ₃ ⁻ , K ₂ SO ₄ , CO ₃ ²⁻
3	black powder	pipe and sand	gray crystalline black granules	K ₂ SO ₄ , CO ₃ ²⁻ unreacted
4	black powder	pipe and building material	gray crystalline black granules	NO ₃ ⁻ , K ₂ SO ₄ , CO ₃ ²⁻ unreacted
5	black powder	room wall	black deposit	NO ₃ ⁻ , K ₂ SO ₄ , CO ₃ ²⁻ , CNS ⁻
6	smokeless, single-base smokeless, single-base	pipe and sand	black cylinders resinous black cylinders	NC, DNT, K ₂ SO ₄ NC, K ₂ SO ₄ , NO ₂ ⁻ unreacted
7	smokeless, single-base	pipe and building material	resinous black cylinders	NC, DNT, (CaSO ₄ ·0.5H ₂ O) unreacted
8	smokeless, double-base		black platelets	NG, NC, K ₂ SO ₄
9	smokeless, double-base	pipe and building material	resinous black platelets	NG, NC, SO ₄ ²⁻ , NO ₂ ⁻ , (Na) unreacted
10	chlorate/sugar		white granular	NaClO ₃ , sucrose
11	chlorate/sugar	pipe and sand	resinous white granular	NaClO ₃ , sucrose, NaCl unreacted



FIG. 4—Pipe bomb fragmentation by (left to right) black powder, single-base smokeless powder, double-base smokeless powder, and 40% dynamite: (top) 1 1/2-in. pipe and (bottom) 2 1/2-in. pipe.

TABLE 3—Analysis of dynamite residues.

Number	Explosive, %	Residue-Bearing Surface	Damage	Microscopic Appearance	Components Identified
12	ammonia 20			granular	EGDN, NG, NH ₄ NO ₃ , NaNO ₃ , S, pulp
13	20	¾-in. plywood	8 by 2½-in. crater	white crystalline paper, black deposit	NG, NH ₄ NO ₃ , NaNO ₃ , Na ₂ SO ₄ (I), NO ₂ ⁻
14	20	⅛-in. steel	folded to U-shape	white crystalline	NaNO ₃ , (Na ₂ SO ₄) _{1-n} , (Na ₂ CO ₃) _m , ^a CNS ⁻
15	ammonia gelatin 40			moist, compact	EGDN, NG, NC, NH ₄ NO ₃ , NaNO ₃ , S, pulp
	60			moist, compact	EGDN, NG, NC, NH ₄ NO ₃ , NaNO ₃ , S, pulp
	75			moist, compact	EGDN, NG, NC, NH ₄ NO ₃ , NaNO ₃ , S, pulp
16	40	2 by 6-in wood	shattered	white crystalline	NG, NaNO ₃ , SO ₄ ²⁻
17	40	¾-in. plywood	9 by 4-in. crater	white crystalline	NG, NC, NaNO ₃ , Na ₂ SO ₄ (I)
18	40	3-in. foam rubber and ½-in. plywood	no crater	white crystalline unreacted 40%	EGDN, NG, NC, NH ₄ NO ₃ , NaNO ₃ , Na ₂ SO ₄ (I)
19	40	carpet and ½-in. plywood	9 by 2½-in. crater	white crystalline paper	NG, NaNO ₃ , Na ₂ SO ₄ (I)
20	40	cloth and ½-in. plywood	9 by 3-in. crater	white crystalline unreacted 40%	NG, NC, NaNO ₃ , Na ₂ SO ₄ (I)
21	40	ceiling tile and ½-in. plywood	6 by 3-in. crater	white crystalline	NG, NaNO ₃ , Na ₂ SO ₄ (I)

22	40 ^b	9 by 12-ft room	9 by 6-in. crater shattered	plaster only	NH ₄ NO ₃ , NaNO ₃ , Na ₂ SO ₄ (I), (plaster)
23	40	wooden box and batteries	shattered	white crystalline black deposit	NaNO ₃ , (Na ₂ SO ₄) _{1-n} , (Na ₂ CO ₃) _n ^a
24	40 ^b	pipe and 9 by 12-ft room	fragmentation shattered	white crystalline	NaNO ₃ , (Na ₂ SO ₄) _{1-n} , (Na ₂ CO ₃) _n ^a
25	40	pipe and 9 by 12-ft room	fragmentation shattered	white crystalline	NG, (Na ₂ SO ₄) _{1-n} , (Na ₂ CO ₃) _n ^a
26	60	¾-in. plywood	9 by 5½-in. crater	white crystalline unreacted 60% paper	EGDN, NG, NC, NH ₄ NO ₃ , NaNO ₃ , SO ₄ ²⁻
27	60	gypsum wallboard and 2 by 6-in. wood	shattered	gypsum	NG, NC, NH ₄ NO ₃ , NaNO ₃ , SO ₄ ²⁻ , (gypsum)
28	60	gypsum wallboard and plastic molding	shattered	gypsum	NG, NC, NH ₄ NO ₃ , NaNO ₃ , Na ₂ SO ₄ (I), CNS ⁻ , (gypsum)
29	75	¾-in. steel	8 by 1-in. dent	white crystalline	NG, NH ₄ NO ₃ , NaNO ₃ , Na ₂ SO ₄ (I), CNS ⁻
30	75 ^c	¾-in. steel	8 by 1-in. dent	white crystalline	NaNO ₃ , Na ₂ SO ₄ (I)
31	60	gelatin		moist, compact	EGDN, NG, NC, NaNO ₃ , pulp, BaSO ₄
32	60 ^d	¾-in. steel	8 by 5-in. crater	white crystalline	NO ₃ ⁻ , NO ₂ ⁻ , Na ₂ CO ₃ ·H ₂ O, Ba

^a n = 0.2 to 0.5.

^b Two sticks.

^c No wrapper paper.

^d No wrapper paper, 1 lb shaped.

TABLE 4—Analysis of plastic explosive residues.

Number	Explosive	Residue-Bearing Surface	Damage	Microscopic Appearance	Components Identified
33	C4			white plastic	plasticizer, RDX
34	C4	¾-in. plywood	10 by 9-in. crater	black deposit	negative
35	C4	¾-in. steel	7 by 3½-in. crater	black deposit	negative
36	C4, PETN booster	¾-in. steel ½-in. plywood placed 12 in. from charge	5 by 8-in. crater shattered	black deposit black deposit	RDX RDX, PETN
37	detonating cord			white plastic	PETN
38	detonating cord 0.45-in. diameter	soil	trench	orange plastic wrapper	negative
39	detonating cord 0.2-in. diameter	aluminum-sheathed wood	cut metal and wood	white fibers from cord	PETN



FIG. 5—*Black powder pipe bomb debris.*

granules of unreacted black powder had not been recognized, then identification of the explosive would have to have been based on the reaction product only.

The single-base smokeless powder consisted of NC cylinders coated with graphite and DNT to control burning. It also contained a small amount of potassium sulfate additive. Numbers 5 through 7 in Table 2 summarize the analyses. Figure 7 illustrates the effect of a cap-initiated pipe bomb in a room corner. No wall push was observed, unreacted explosive was thrown around the room, and a devastating fire was started within the wall.

The double-base smokeless powder consisted of graphite-coated NG and NC, plus a small amount of potassium sulfate additive. Numbers 8 and 9 in Table 2 summarize the analyses. A flame-initiated, 0.5-lb charge in a room showed wall push, blew out the windows, but left intact a light bulb in the ceiling. Of twelve fragments recovered from the crater and walls, five bore unreacted explosive. All fragments showed fresh rusty areas and traces of resinous residue. NG and NC were identified by IR and TLC. Aqueous extraction gave a low yield of contaminants in which sulfate was identified by

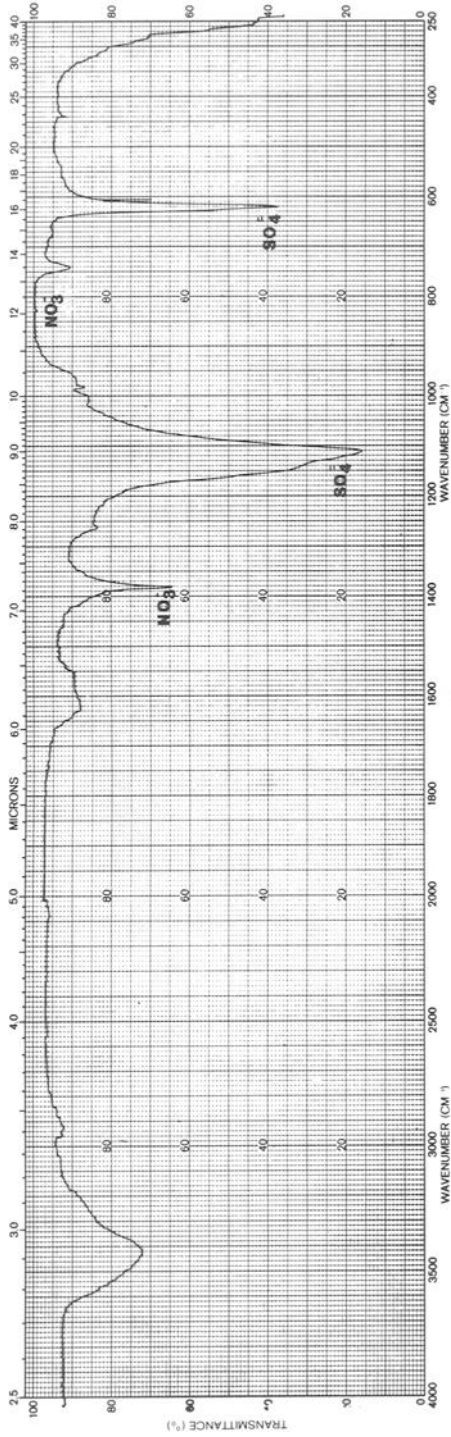


FIG. 6—Black powder residue. IR spectrum of aqueous extract (K_2SO_4 , KNO_3).

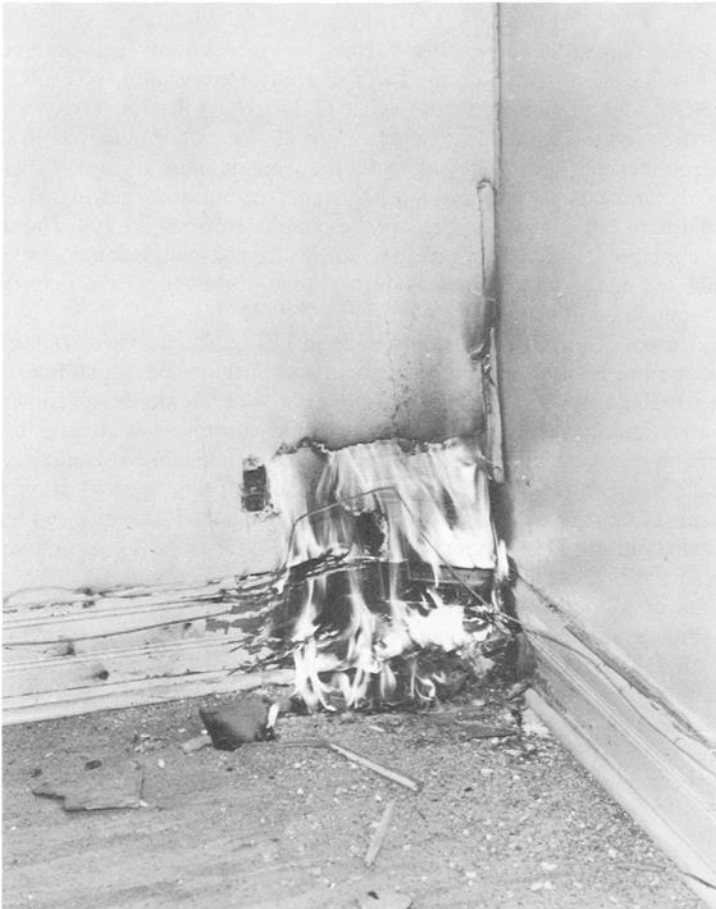


FIG. 7—*Single-base smokeless powder pipe bomb debris.*

IR and sodium by spectrography. Spot tests showed nitrate, nitrite, ammonium, and chloride. The X-ray powder pattern was not identified. The danger of reliance on chemical tests is apparent, since if analysis consisted only of TLC and of spot tests for sodium, nitrate, and ammonium, then in the absence of unreacted explosive the examiner could be misled toward dynamite; that is, the analysis would appear to be NG, NC, NH_4^+ , Na, and NO_3^- , of which three are the result of contamination from the surroundings. The range of instrumental analysis applied in Fig. 1 should prevent this type of error, since all dynamite aqueous extracts were identified by X-ray powder diffraction.

Chlorate/sugar produced a fireball and explosion on flame initiation. Unreacted explosive was recovered. Pipe fragments bore brown gummy residue and fresh rust spots. Analyses are summarized in Table 2, Nos. 10 and 11. Extraction yielded unreacted sugar and sodium chlorate identified by IR, and the sodium chloride product identified by polarizing microscopy and X-ray powder diffraction. Since sodium chlorate is also isotropic, the polarizing microscope was well suited to this analysis. Potassium chlorate is anisotropic.

High Explosives

Dynamite—Dynamite is the explosive class most commonly encountered in bomb incidents. The classes of dynamite used in this study were gelatin (NG, NC), ammonia (NG, NH_4NO_3), and ammonia gelatin (NG, NC, NH_4NO_3). In our service area and elsewhere, "nitroglycerine" dynamites contain up to 85% ethylene glycol dinitrate (EGDN) with the nitroglycerine. The EGDN depresses the freezing point of the NG, which lessens the risk of dynamite becoming unstable through freezing and thawing. The EGDN is more volatile than NG and is the basis of "dynamite sniffers" [1,10]. The dynamite in this study contained sodium nitrate and sulfur for oxygen balance, except for the gelatin which did not contain elemental sulfur. None of these dynamites contained DNT, but it is a common additive.

Cook [12] predicts that dynamite with sodium nitrate should yield sodium carbonate and that in the presence of sulfur, coproducts may include sodium sulfide, sulfite, and sulfate, depending on the oxygen balance. For the ammonia gelatins, calculated products are primarily sodium sulfate and sodium carbonate in a ratio in which the sodium carbonate percentage increases as the explosive percentage strength decreases [19].

These data point to TLC and X-ray diffraction as prime identification techniques. Following the TLC work of Jenkins and Yallop [9], this study commenced with benzene eluent, but this did not cleanly separate EGDN and NG. Good separation was achieved by benzene/hexane eluent [29] and this system superseded benzene.

The results of a comparative study of TLC solvent systems on 250- μm silica gel G plates are shown in Table 5. R_f values are similar to those reported by Jenkins and Yallop [9] on 250- μm silica gel G, but are about two times less than R_f values reported by Hoffmann and Byall [10] on 200- μm silica gel G. This discrepancy is presumably due to the difference in thickness of the silica gel layer and underlines the necessity for running fresh standards with every TLC. Table 5 indicates that chloroform/acetone (1/1) is the best system for initial TLC analysis of an unknown. Ammonium and nitrate

TABLE 5—TLC systems employed for explosive analysis.

Explosive	TLC Systems					
	Benzene	Benzene: Hexane 1:1	Xylene: Hexane 3:2	CCl_4 : $\text{C}_2\text{H}_4\text{Cl}_2$ 4:1	Acetone: CHCl_3 1:1	Ethanol
EGDN ^a		0.23	0.31	0.23		
NG ^a	0.38	0.17	0.21	0.16	0.65	0.64
NC ^a	0	0	0	0	0	0
PETN ^a	0.37	0.15	0.21	0.12	0.71	0.60
RDX ^a	0	0	0	0	0.46	0.49
DNT ^b	0.37	0.17	0.22	0.20	0.63	0.65
TNT ^b	0.40	0.20	0.30	0.15	0.67	0.61
NO_3^- ^{c*}						0.57
NH_4^+ ^d						0.13

^a NaOH/Griess, 250- μm silica gel G.

^b TiCl_3 /DMAB, 250- μm silica gel G.

^c $\text{Ph}_2\text{NH}/\text{H}_2\text{SO}_4$, 250- μm silica gel G.

^d EtOH/Nessler, 250- μm silica gel G.

* NaNO_3 , KNO_3 , NH_4NO_3 .

ions migrate at different rates and sodium, potassium, and ammonium nitrates are not distinguishable by developing nitrate only. This has been overlooked in previous publications on explosive residue analysis. Ammonium ion was conveniently developed using the Nessler reagent [13].

Thus, to characterize dynamite by TLC, a minimum of three systems was employed: benzene/hexane with NaOH/Griess for EGDN, NG, and NC; ethanol with $\text{Ph}_2\text{NH}/\text{H}_2\text{SO}_4$ for NO_3^- ; and ethanol/Nessler for NH_4^+ .

Table 3 summarizes the results of 18 dynamite explosions. Unless otherwise noted, the charge was one 8 by 1/4-in. stick. The results are discussed by class.

Ammonia Dynamite—Explosions were conducted with one 8 by 1/4-in. stick on wood and one deteriorated 8 by 1/4-in. stick on steel. The results are summarized in Table 3, Nos. 13 and 14, and clearly demonstrate the complexity of explosive residue analysis.

In both cases a white crystalline residue was observed, but this was not recognizable as unreacted dynamite. Acetone extraction and TLC identified NG in the wood crater fragments but neither on the wood crater surroundings nor on the steel. Aqueous extraction yielded white crystals, the IR spectrum of which showed the presence of sulfate and carbonate products in addition to unreacted nitrate. The relative proportions in the IR varied as shown below, where s is strong, w is weak, and m is medium.

wood crater fragments	SO_4^{2-} (s)	CO_3^{2-} (w)	NO_3^- (w)
wood crater surroundings	SO_4^{2-} (m)	CO_3^{2-} (w)	NO_3^- (s)
steel	SO_4^{2-} (s)	CO_3^{2-} (m)	NO_3^- (m)

X-ray powder diffraction of the mixture [30] identified the product from the wood as $\text{Na}_2\text{SO}_4(\text{I})$ and that from steel as sodium carbonate sulfate (see Table 6). The IR spectrum of sodium carbonate sulfate is illustrated in Fig. 8 (steel residue) and the morphology in Fig. 9. These products are further discussed in Appendix B. The nitrate in each case was identified as the unreacted sodium salt by X-ray powder diffraction and the polarizing microscope. No ammonium ion was found in the wood debris and was noted only by spot test screening in the steel extract.

That the same explosive gives different products on unconfined detonation is best explained by the deterioration of one stick. The product composition is apparently determined by the mole ratio of $\text{CO}_3^{2-}:\text{SO}_4^{2-}$. These results show the major drawback to solvent extraction in that sodium sulfate and sodium carbonate might have been present independently, but are isolated from a complex aqueous system as a solid solution (see Appendix B).

Ammonia Gelatin Dynamite—The velocity of 40% Forcite® is around 7000 feet per second (fps) unconfined and 13,000 fps confined. Velocities are proportionately higher for 60% and 75%. The variation of velocity with confinement is typical of gelatin dynamites [31]. Figure 10 shows the increased shattering effect of an 8 by 1/4-in. stick of explosive on 3/4-in. plywood as the velocity increases from 6000 to 25,000 fps. The explosives illustrated were 20, 40, and 60% dynamite, and C4, respectively (Table 3, Nos. 13, 17, 26; Table 4, No. 34). Tests in residential premises showed a marked contrast to the low explosives. Walls were shattered, as opposed to pushed, and the reverse blast brought window glass back into the rooms. Figure 11 shows damage caused by two sticks of unconfined 40% Forcite® in a 9 by 12-ft room (Table 3, No. 22). When confined in pipes, some pipe fragments passed through several walls and doors.

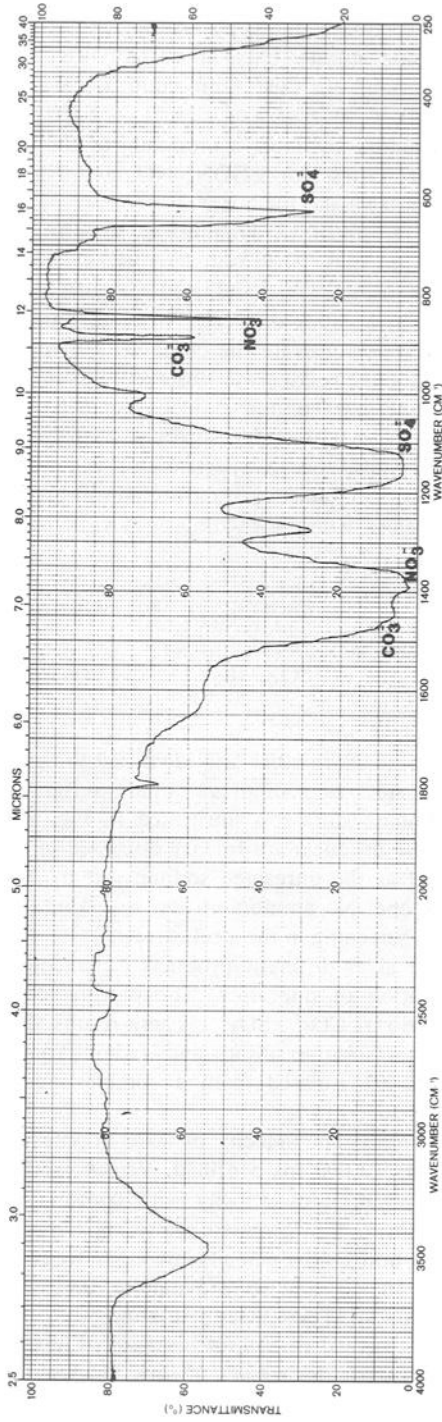


FIG. 8—20% dynamite, IR spectrum of aqueous extract from steel (sodium carbonate sulfate, NaNO_3).

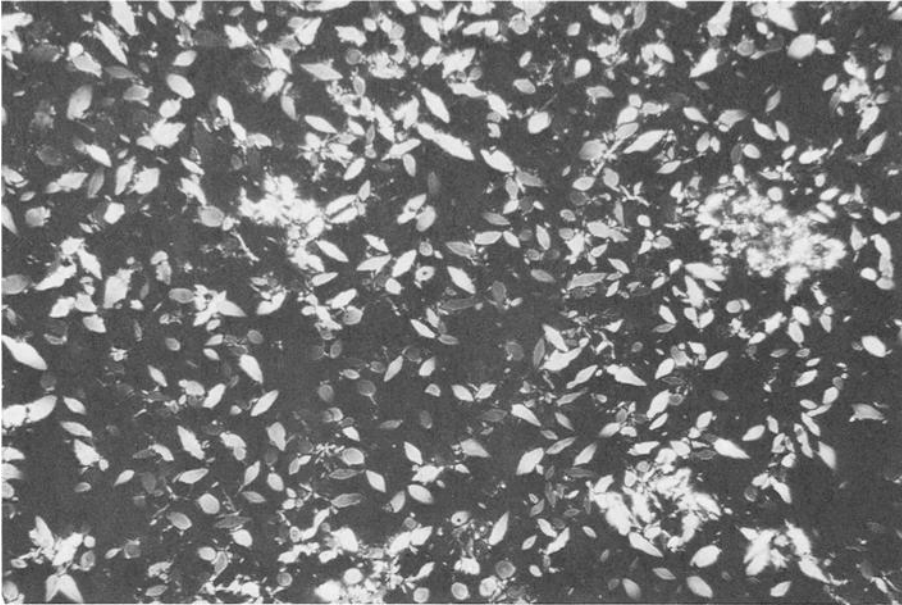


FIG. 9—Sodium carbonate sulfate in aqueous extract of explosive residue (crossed polars, original magnification $\times 250$).

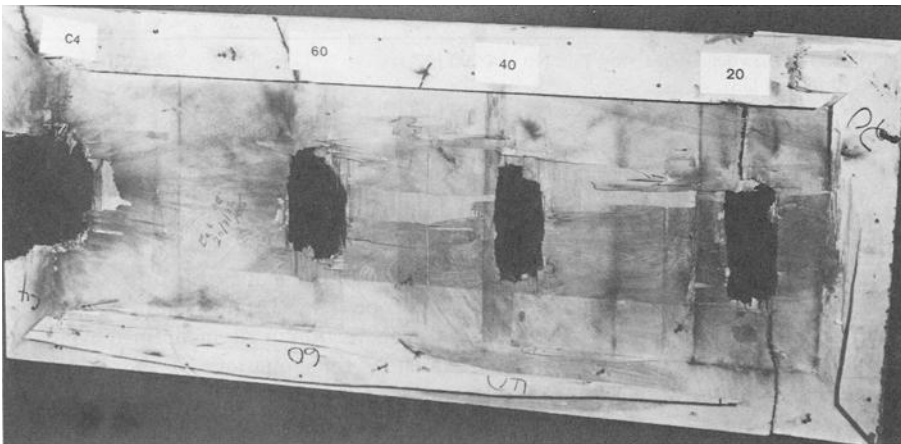


FIG. 10—Damage by a unit charge of 20, 40, and 60% dynamite and C4.

Numbers 16 through 30 in Table 3 summarize the test explosions of this class. In only three instances (Nos. 18, 20, 26) was unreacted explosive recognized in the debris.

The confined explosives, Nos. 23 through 25, were distinguished from the unconfined explosives by the composition of the reaction product as determined by X-ray powder diffraction. The confined explosives gave sodium carbonate sulfate, whereas the unconfined gave $\text{Na}_2\text{SO}_4(\text{I})$. Unlike 20% stumping powder, unconfined Forcite[®] residue

TABLE 6—X-ray powder diffraction data of sodium carbonate sulfates.

Na ₂ SO ₄ (I) ^a		2Na ₂ SO ₄ ·Na ₂ CO ₃ ^b		2Na ₂ SO ₄ ·Na ₂ CO ₃ ^c		(Na ₂ SO ₄) _{1-n} (Na ₂ CO ₃) _n ^d	
d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀	d, Å	I/I ₀
						9.20	10
4.60	10	4.60	20			4.51	20
3.87	63	3.85	90	3.88	70		
				3.78	80	3.798	70
3.56	40	3.55	70	3.51	70	3.530	50
						3.444	10
						3.076	20
2.82	100	2.80	100	2.78	100	2.795	100
2.66	100	2.66	100	2.64	70	2.645	60
				2.58	80	2.587	60
						2.479	5
						2.348	10
2.30	2	2.30	10			2.302	5
2.19	8	2.18	50				
2.13	1			2.13	30	2.149	20
				2.10	30	2.106	1
				1.97	10	1.980	10
1.93	40	1.92	90	1.93	40	1.932	30
				1.89	40	1.903	30
1.78	8	1.77	50	1.75	30	1.765	20
						1.740	5
				1.62	5		
1.57	10	1.56	40				
1.54	7	1.53	20				
				1.50	10		

^a ASTM Powder Diffraction File No. 1-0990 [27].

^b Ramsdell [33].

^c ASTM Powder Diffraction File No. 2-0840 [27].

^d This study.

showed no carbonate in the IR (Fig. 12). The presence of some carbonate was inferred, however, from effervescence with acid. There was insufficient sodium nitrate in the confined explosive residue for identification in the X-ray powder pattern, but it was recognizable in the bulk sodium carbonate sulphate matrix by orthoscopic and conoscopic observation with the polarizing microscope (Nos. 23 and 24).

Sodium nitrate was identified by X-ray powder diffraction in all unconfined explosions and NG was identified by TLC in approximately three-quarters of the explosions. However, ammonium nitrate and NC were detected in only 47 and 40% of the tests, respectively. In the TLC systems tested, NC had an R_f value of 0, in common with many solvent-extracted contaminants which often develop a yellow color with Griess reagent and possibly mask NC. Where a TLC system was used which separates EGDN and NG, (Nos. 17, 18, 22 through 28, 30) EGDN was found in only one-third of the cases in which NG was identified. This cautions against complete reliance on a dynamite sniffer to detect residue.

IR prior to TLC of ether and acetone extracts detected explosive components in 50% of the tests, as opposed to 80% for TLC. In some TLC analyses, contamination reduced the R_f value of explosive components relative to standards, and in these cases IR aided interpretation.



FIG. 11—40% Forcite® debris (two sticks, unconfined).

No consistent difference in residue composition was found between Forcite® 40, 60, or 75%, notwithstanding their calculated products being in varying proportions. The complexity of the $\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$ aqueous system complicates this issue. For 60 and 75% Forcite® the yield of sulfate product was minor compared to sodium nitrate, but as No. 16 shows, this is not a consistent difference from 40% Forcite®.

Explosions of 75% Forcite® with and without wrapper paper (Nos. 29 and 30) showed little difference in products, although CNS^- was detected with paper only. CNS^- was also a product of black powder (No. 4), 20% dynamite (No. 14), and 60% Forcite® (No. 28).

The effect of contamination was not serious, although sodium chloride of unknown origin was often noted. Gypsum plaster in particular was noted in some X-ray powder patterns but did not prevent identification of product sulfate in No. 28. Figure 13 shows the IR spectrum of the aqueous extract from No. 27, 60% Forcite® on gypsum wall-board, in which sulfate product is identified by a peak at 615 cm^{-1} . Its low yield precluded further identification from the X-ray powder pattern.

In summary, out of 15 explosions of ammonia-gelatin dynamite, 5 residues could be classed as being from ammonia-gelatin dynamite (Nos. 18, 20, 26 through 28), 2 from ammonia dynamite (Nos. 22, 29), 1 from gelatin dynamite (No. 17), and 7 from dynamite (Nos. 16, 19, 21, 23–25, 30).

Gelatin—One pound of a 5-lb stick of seismic dynamite was shaped and detonated

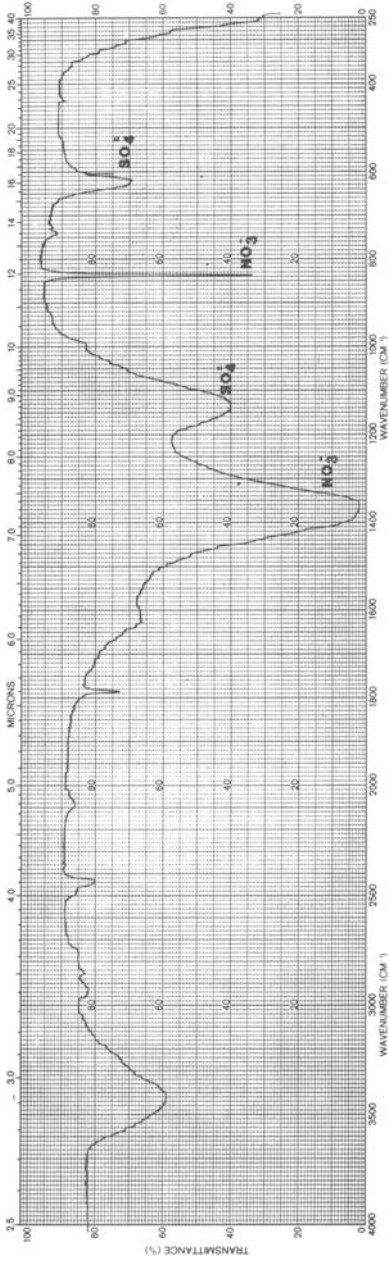


FIG. 12—40% Forcite® unconfined, IR spectrum of aqueous extract from carpet (Na_2SO_4 (I) and NaNO_3).

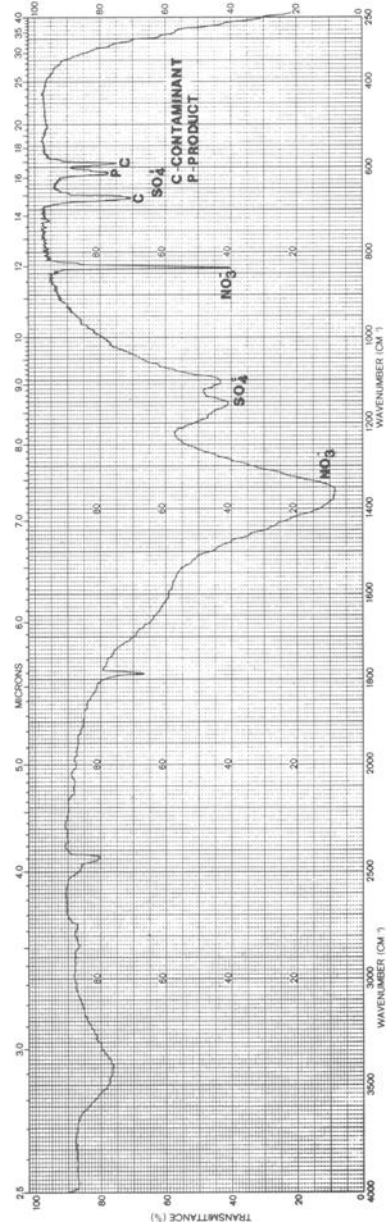


FIG. 13—60% Forcite® unconfined, differentiation of sulfates by IR analysis [NaNO_3 ; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (contaminant); sodium sulfate (product)].

on steel (Table 3, No. 32). A heavy white crystalline residue was largely sodium carbonate. This residue could not be classed as being from gelatin dynamite since NC was not recovered, but the identification of sodium carbonate indicates that the dynamite contained no elemental sulfur and again stresses the value of product identification by instrumental analysis. The presence of barium was shown spectrographically in the insoluble material, which emphasizes the value of systematic analysis.

Plastic C4—The velocity of C4 is around 25,000 fps. C4 was detonated by either blasting cap or detonating cord booster. No unreacted explosive was observed in the characteristic black deposit. The analyses are summarized in Table 4, Nos. 34 to 36. In only one out of three explosions (No. 36) was RDX identified by TLC. On one piece of debris, PETN from detonating cord booster was also identified.

Detonating Cord—The detonating cord was charged with PETN. In one of two explosions (Table 4, Nos. 38 and 39) PETN was identified by TLC. In both cases traces of wrapper were recovered.

General

The analytical scheme in Fig. 1 was derived from practical experience and the chemical literature and uses the instruments routinely used in Royal Canadian Mounted Police (RCMP) laboratories. It is not an absolute and is adapted as conditions demand. For example, ether would not be used to extract residue from an engine block. Similarly, if volatile liquids such as nitrobenzene or gasoline were suspected, then high vacuum techniques, vapor phase IR, and gas chromatography would be applied. The test explosions were part of a series of workshop seminars run by our laboratory for training purposes, and involved police and fire investigators and IED specialists in addition to laboratory personnel.

The analytical results show that the scheme permitted correct classification of the explosives, although subclassification of dynamite was not always achieved. Unreacted explosive in debris was recognized by microscopic examination for most of the low explosives, few of the dynamites, and none of the plastic explosives. The value of explosive product identification has been demonstrated and within the ammonia-gelatin series it distinguished confined and unconfined dynamite. Residue composition and distribution were not uniform and the most comprehensive recoveries were, not surprisingly, made from the crater area, which receives a potential hemisphere of blast.

The most useful techniques were microscopy, TLC, X-ray powder diffraction, and infrared spectroscopy. The emission spectrograph replaced spot tests for metals. Spot tests provided rapid screening of a high yield of residue, but were usually relegated to checking for components missed by the other techniques. A negative spot test was often given more weight than a positive test. However, a spot test solution as a TLC developer was very useful and greatly enhanced specificity.

Calcium sulfate building products, ammonium chloride from batteries, sodium chloride of unknown origin, and resins were the contaminants most often encountered by solvent extraction, but they did not preclude residue identification in the test series.

Table 7 summarizes the components identified in this study and illustrates how results may be interpreted in analysis of an unknown. The scheme has been routinely applied to casework with satisfactory results.

Summary

A scheme for systematic analysis of explosive residues is presented and demonstrated

TABLE 7—Explosive components identified and their sources.

Component	Probable Origin
NaNO ₃	dynamite
NH ₄ NO ₃	ammonia dynamite, blasting slurry
KNO ₃	black powder
K ₂ SO ₄	black powder, safety fuse, smokeless powders
Na ₂ CO ₃	dynamite
Na ₂ SO ₄ (I)	dynamite
(Na ₂ SO ₄) _{1-n} (Na ₂ CO ₃) _n	dynamite
NaClO ₃	chlorate
KClO ₃	chlorate
NaCl	NaClO ₃ , "permitted" dynamite, contaminant
KCl	KClO ₃
NH ₄ Cl	dry cell battery, "permitted" dynamite
NO ₃ ⁻	dynamite, black powder
NO ₂ ⁻	smokeless powders, dynamite
NH ₄ ⁺	ammonia dynamite, NH ₄ NO ₃ blasting slurry, dry cell battery
CNS ⁻	black powder, dynamite
CO ₃ ²⁻	dynamite
SO ₄ ²⁻	dynamite, black powder, smokeless powder
Cl ⁻	dry cell battery, "permitted" dynamite, contaminant
Na	dynamite, contaminant
K	black powder
Ca	contaminant, dynamite
B	dynamite
Ba	dynamite
Pb	blasting cap residue
Al	blasting cap casing
Zn	dry cell battery casing
EGDN	dynamite
NG	dynamite, double-base smokeless powder
NC	dynamite, single-base smokeless powder
TNT	blasting slurry, military demolition charge
DNT	dynamite, single-base smokeless powder
PETN	detonating cord
RDX	C4 plastic explosive

by test explosions using commercial, military, and homemade explosives. The significance of reaction product identification is demonstrated.

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APPENDIX A

Glossary of Explosive Abbreviations and Terminology

Black Powder—KNO₃/C/S, usually 75/15/10

- Blasting Cap**—A small high explosive charge in a metal cylinder, used to initiate a bulk high explosive charge by means of a shock wave; initiated electrically or by safety fuse
- Booster**—A small high explosive charge used in conjunction with a blasting cap to ensure detonation of a bulk high explosive charge
- C**—Carbon
- C4**—Military code for plastic explosive based on RDX
- Chlorate/Sugar**—Mechanical mixture of potassium or sodium chlorate and sugar
- Detonating Cord**—A linear explosive consisting of a series of cylindrical wrappings with a central high explosive core, usually PETN
- DNT**—2,4-dinitrotoluene, $C_7H_6(NO_2)_2$
- EGDN**—Ethyleneglycol dinitrate, $C_2H_4(ONO_2)_2$
- Forcite**[®] —Trade name for dynamite (Canadian Industries Ltd.)
- Geogel**[®] —Trade name for dynamite (Canadian Industries Ltd.)
- High Explosive**—Explosive with a velocity of detonation greater than 3280 ft/s, for example, dynamite and plastic explosive
- IED**—Improvised explosive device
- KNO₃**—Potassium nitrate
- Low Explosive**—Explosive with a velocity of detonation less than 3280 ft/s, for example, black powder and pistol and rifle smokeless powder propellants
- NaNO₃**—Sodium nitrate
- NC**—Nitrocellulose, variable formulation
- NG**—Nitroglycerine, $C_3H_5(ONO_2)_3$
- NH₄NO₃**—Ammonium nitrate
- PETN**—Pentaerythritol tetranitrate, $C_5H_8(ONO_2)_4$
- Plastic Explosive**—High explosive plus plasticizer to enable shaping of the charge, for example, C4
- Polar**[®] —Trade name for dynamite (Canadian Industries Ltd.)
- RDX**—Research and development explosive, cyclotrimethylenetrinitramine, $C_3H_6N_3(NO_2)_3$
- S**—Sulfur
- Safety Fuse**—A series of cylindrical wrappings with a black powder core which burns at a constant rate, usually 40 s/ft
- Smokeless Powder (double base)**—Propellant based on nitrocellulose and nitroglycerine
- Smokeless Powder (single base)**—Propellant based on nitrocellulose
- TNT**—2,4,6-trinitrotoluene, $C_7H_5(NO_2)_3$

APPENDIX B

$Na_2SO_4(I)$ is a metastable form of sodium sulfate which is stabilized by carbonate [27,32]. Sodium carbonate sulfate is reported as the rare mineral burkeite [27] and as a synthetic material [33] isolated from the sodium carbonate/sodium sulfate aqueous system [34]. Sodium carbonate sulfate was synthesized in our laboratory by evaporation of an aqueous solution of sodium sulfate and sodium carbonate, with a sodium carbonate mole ratio of 0.2 to 0.5. The X-ray powder pattern in this range showed neither precursor and, due to isomorphous exchange of carbonate and sulfate [33], showed no difference in *d*-spacings or intensities. Comparative *d*-spacings are given in Table 6 for variously reported sodium carbonate sulfates. Our synthetic material was indistinguishable from the carbonate sulfate residues noted in Table 3, Nos. 14 and 23 through 25.

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