

Identification of Dynamite Explosives in Post Explosion Residues

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ABSTRACT: The investigation of post blast residues of dynamite explosives with respect to the behavior of nitro-aromatic compounds is described. Experimental blasts were performed with free hanging charges. The samples taken from metal plates placed at different distances from the center of the explosion were analyzed by GC-TEA. The results were evaluated with respect to the relative amounts of the dinitrotoluene isomers to each other. The portions of the dinitrotoluenes showed good correspondence in the post blast residues with the original explosives.

KEYWORDS: criminalistics, commercial explosives, dynamite explosives, experimental blasts, explosives trace analysis, nitro/nitrospecific detection

Dynamite explosives are the most complex mixtures among the commercial explosives. In addition to the ammonium nitrate and one or two fuel components, as in the commercial blasting explosives, the European dynamites also contain explosive oils, nitro-aromatic compounds, additional nitrates, woodmeal, nitrocellulose, dyes and trace amounts of ingredients that are special for each manufacturer [1]. The identification of the brand or the comparison with other explosives is only possible if characteristic ingredients of the dynamite are found, even in the post blast residues. The manufacturer's typical compounds are often unknown to others or usually can not be found in the post explosion residues. Also, nitrocellulose, dyes and woodmeal cannot be analyzed in the debris from a bomb scene. The explosive oils, nitroglycerine (NG) and/or ethyleneglycol dinitrate (EGDN), are found at a bomb scene, but their presence is only characteristic to a dynamite explosive, but not to identify the brand. These problems of analyzing post blast residues are especially difficult in the case of slurry or emulsion explosives [2], where usually no nitro-compounds are present.

A possibility for identifying the brand of European dynamites can be found with the nitro-aromatic compounds, usually dinitrotoluene (DNT) and trinitrotoluene (TNT). They can be detected in very small amounts and very selectively in the complex composition of extracts from the debris. An individual identification feature for any dynamite can be found in the relative amounts of the nitro-aromatics to each other. The ratio of the different isomers of DNT depend on the production process and may give information on the brand of the dynamite.

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In order to identify an explosive in the post blast residues by the relative amounts of isomers, the ratios between the selected compounds must remain unchanged. Two basic problems arise because of two interfering effects. First, the different reactivity of the constituents leads to a change of the composition in the residue, especially for the less reactive inorganic salts [3]. Secondly, the heat of explosion leads to the evaporation of all explosive residues. The lower evaporating constituents are partly lost when the explosion gases condensate at cold surfaces. Therefore it is better to consider only the compounds with similar vapor pressures and similar reactivity.

In this paper the analysis of explosives residues from experimental blasts is described. Whether it is possible to identify a dynamite by determination of the ratios of the nitro-aromatic constituents was investigated.

Experimental Section

Cotton Swabs

Cotton swabs produced for eye cleansing were purchased from Kalff (Euskirchen, Germany). The new swabs were first washed by Soxhlet extraction with acetone for 8 h.

Sample Preparation of the Explosive Residue

The explosive residues from experimental blasts were collected with acetone-wetted cotton swabs. The cotton swabs were extracted with 40 mL acetone in an ultrasonic bath for about 15 minutes. The extracts were filtered through one-way filters (0, 2 μ m) to remove particles. The acetone was evaporated at a temperature of 35°C and under a light nitrogen flow (20–30 minutes).

Sample Preparation of the Original Explosives

Two to three g of each dynamite explosive were extracted with 40 mL diisopropylether in an ultrasonic bath for 10 minutes. The resulting ether was then decanted into a vapor bowl. The extraction procedure was repeated three times. Only organic explosive components can be dissolved in diisopropylether, so that the nitro-aromatics and the explosive oils are in the ether extract, whereas the inorganic constituents are in the rest. After evaporating the ether at ambient temperature, the residue was dissolved in a defined amount of acetone and the extract was filtered. The inorganic constituents were dried, weighed, and dissolved in distilled water. The insoluble components such as woodmeal and nitrocellulose were filtered out before determining the anions by IC. The analysis of ammonium was performed by titration.

Chromatography

The gas chromatograph used was a Varian 3400 with split/splitless injection coupled to a thermal energy analyzer (TEA) from Thermedics. The TEA was modified as described in [4]. GC column was a 12m DB 5 capillary (0.25 μm i.d.).

Results and Discussion

All the data, that are listed in this paper, were gathered following a fixed operational scheme. Six German dynamites were selected and their composition was analyzed. The selected dynamites were detonated as free hanging charges. Residues were collected by swabbing the metal plates that were arranged at pre-determined distances. The swabs were extracted in the laboratory and the extracts were analyzed by gas-chromatography with chemiluminescence detection (GC-TEA) [5]. GC/MS would also be well suited for the intended purpose [6], but only confirmations were performed during the work described in this paper. GC/MS can analyze traces of nitro-aromatics at very low levels together with structural information by GC/MS [7].

Selected Dynamites

The dynamites were two powdery (nongelatinous) and four gelatinous dynamites. The content of explosive oils, primarily EGDN, was determined only qualitatively. A quantitative analysis was performed on the ammoniumnitrate and on the nitro-aromatic constituents. The results of the chemical analysis are listed in Table 1. The DNT is split into the two main isomers, the 2,4-DNT and the 2,6-DNT. The highest amount of EGDN is in Geosit 3 (>30%), lower amounts are in Ammongelit 2 and 3 (20 to 30%), and fairly low amounts are in Donarit 1 and 4 (5 to 10%).

Experimental Blasts and Sampling

The dynamites were exploded in the special arrangement shown in Fig. 1. This arrangement was done so that defined surface areas with an inert and smooth material (steel plates) were at a fixed distance. At these surfaces the residues moving away from the center of the explosion are trapped and can be collected very easily by a simple swabbing procedure. In every experiment the ignition was made at the backside of the charge at the farthest distance relative to the plate. The direction of the ignition is important, because it influences the preferable direction of the expansion of the explosion gases.

The sampling was performed with acetone wetted cotton swabs. The swabs were rubbed over the metal plates and all material was collected. After sampling, the swabs were dried at ambient temperature under a light flow of clean air. During the swabbing procedure very small particles from the original explosive were

found. At distances farther than 5 m, that was the only visible effect on the metal plates. If the plates were arranged at shorter distances (2.5 m), there was a gray coating on the surface in addition to some small particles. At a distance of 1 m, no particles from the original explosive were visible, but the surface was roughly damaged. A photograph of one such small particle found after the detonation in 5 m distance is shown in Fig. 2. Obviously it is nitrocellulose, which can also be found as transparent particles in the original dynamite. The chemical analysis of the nitro compounds in that nitrocellulose particle is listed in Table 2 and compared to the analysis of the original explosive. To compare the values, the results were normed to the content of 2,4-DNT. The normalization was made by calculating the ratio of each substance to the 2,4-DNT in the same sample. The correspondence between the original and the particle is pretty good with the exception of the EGDN. The amount of EGDN in the particle is lower than expected because it is lost very easily because its high vapor pressure.

Relative Amounts of Nitro-Aromatics in Post Blast Residues

The swabs from the metal plates in different distances were extracted with acetone and investigated by gas-chromatography with chemiluminescence detection. GC-TEA was selected in order to have a very sensitive and specific method for the analysis of the nitro-components. Figure 3 shows the chromatogram of a post explosion analysis compared to the chromatogram of the original explosive. The presence of all the nitro-compounds in the residue can easily be recognized. The GC analysis has a very good resolution for the individual isomers of DNT. These are 2,4-DNT, 2,6-DNT, 2,5-DNT, 2,3-DNT, 3,4-DNT and 3,5-DNT. All these isomers are formed during the technical synthesis of DNT. The proportions for each isomer are listed in Table 3 as given in the literature [8] for the synthesis from pure toluene and o-, m-, or p-nitrotoluene.

If an unknown dynamite appears in the analysis, a detailed investigation is necessary. The absolute amounts of the constituents depend on the total amount of sample including the matrix, so that it is necessary to have an internal standard to compare different samples. From the chromatogram, the ratios for each compound to one fixed compound can be calculated. It is obvious to select the 2,4-DNT, which is the main DNT isomer. The identification of the residues can be accomplished by comparing the data with those of a presumed dynamite or by searching a data base. Data for one dynamite relative to the distance from the center of the explosion is listed in Table 4. In that instance the DNT isomers were only detectable as distinct peaks in the samples from closer distances. Geosit 3 is an explosive that did not reproduce well in the post-blast analysis. If a comparison with bulk explosive is attempted, at least two samples (from different distances) containing distinct amounts of isomers must be found. Other dynamites gave clear results up to 10 m in distance. If all six of the mentioned dynamites are considered, the 2.5 to 5 m distance is the best location to get valuable results. In Figs. 4–9, comparisons are made between the ratio of DNTs in the investigated original explosives and their residues at a fixed distance. The obtained values are scattered around the value of the original explosive. If such results are discussed, all the DNTs have to be regarded. Together, with the findings of the TNT and the qualitative presence of NG or EGDN, a decision about the brand should be possible. Figure 10 shows such a comparison, where the values of a post blast dynamite sample are illustrated together with the analysis of original explosives. Analyzing the data the correct explosive can be identified.

TABLE 1—Chemical analysis of the dynamites (% w/w).

Explosives	Nitrate	Ammonium	TNT	2,4-DNT	2,6-DNT
Donarit 1	55.60	16.70	12.80	0.10 ^a	0.018 ^a
Donarit 4	52.00	18.80	1.70	0.10 ^a	0.010 ^a
Gealmon 22	45.40	14.40	—	2.09	0.71
Geosit 3	35.50	11.10	—	0.71	0.19
AG 2	39.60	13.20	6.60	2.62	0.58
AG 3	45.00	10.90	5.20	2.47	1.23

^aTraces of DNT.

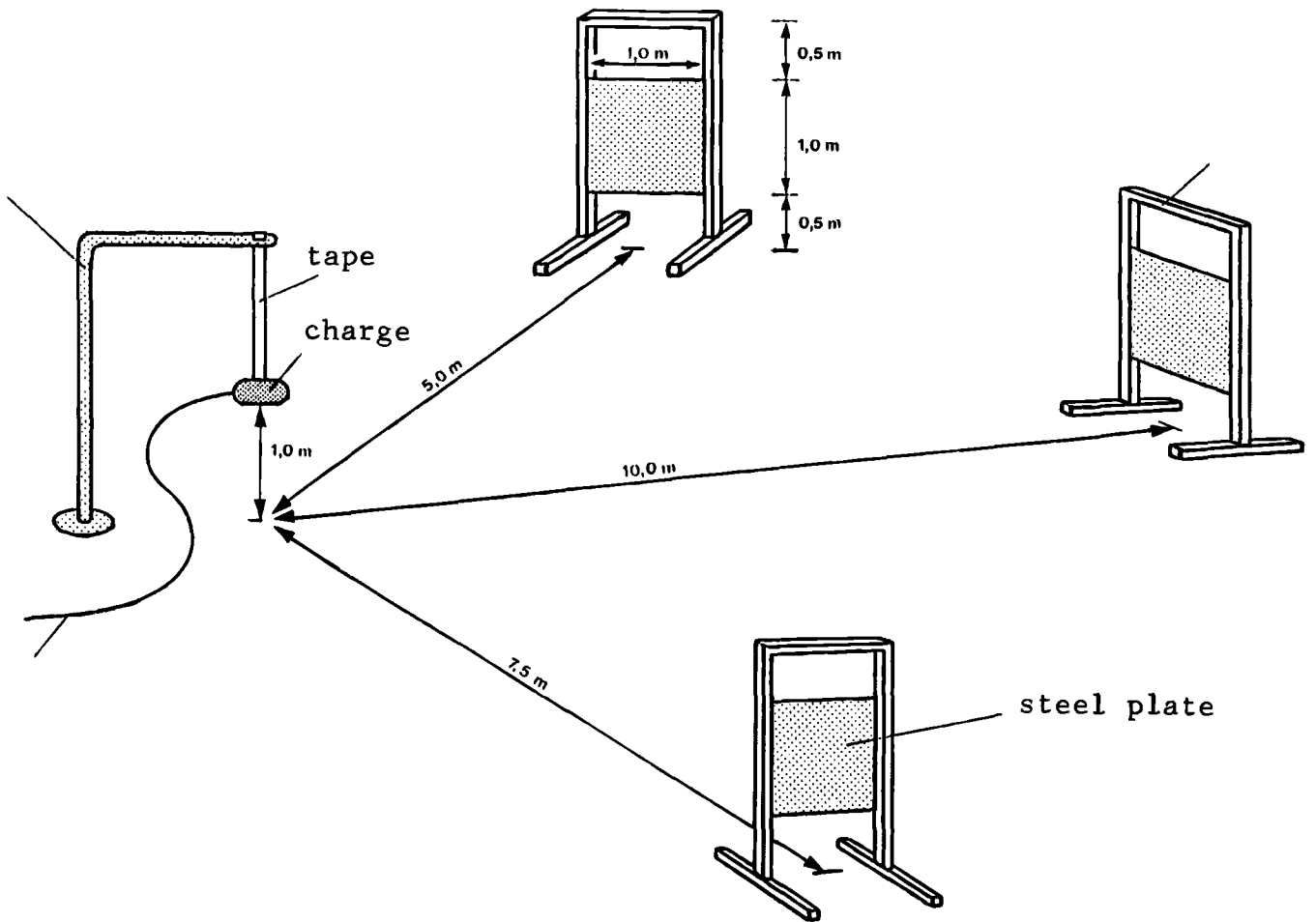


FIG. 1—Arrangement for the experimental blasts.

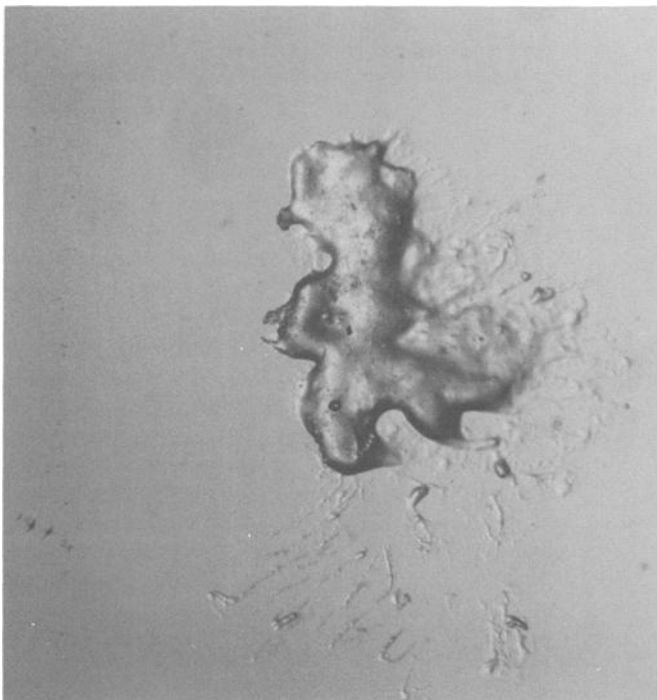


FIG. 2—Particle found at 5 m distance from the explosion. Original magnification 25X.

TABLE 2—Composition of a residue particle.

	Original	Residue
EGDN	3.27	0.74
NG	2.13	2.57
2,6-DNT	0.50	0.43
2,5-DNT	0.05	0.04
2,3-DNT	0.15	0.14
2,4-DNT	1.00	1.00
3,4-DNT	0.30	0.29
TNT	1.60	1.39

TABLE 3—Weight-% of DNT by synthesis.

Starting material	2,3-DNT	2,4-DNT	2,5-DNT	2,6-DNT	3,4-DNT
Toluene	1.3	78	0.5	18	2.4
o-Nitrotoluene	—	67	—	33	<0.5
m-Nitrotoluene	25	—	20	—	55
p-Nitrotoluene	—	99	—	—	—

In actual cases in our laboratory, a dynamite explosive was used containing some special nitro-compounds such as nitronaphthalene and nitroxylenes. If such substances are detected, the identification can be easier, but such obvious results are very rare.

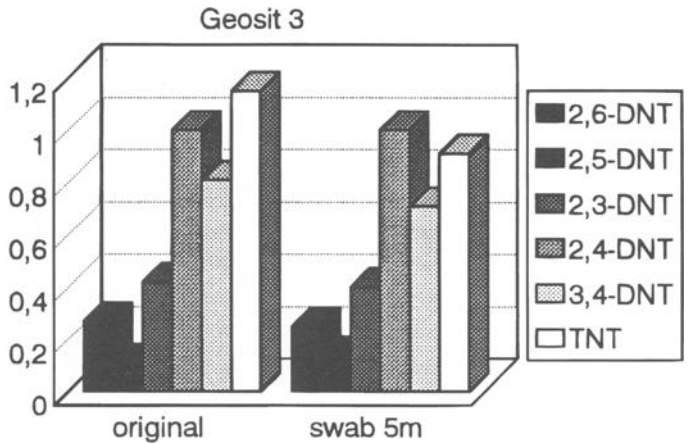
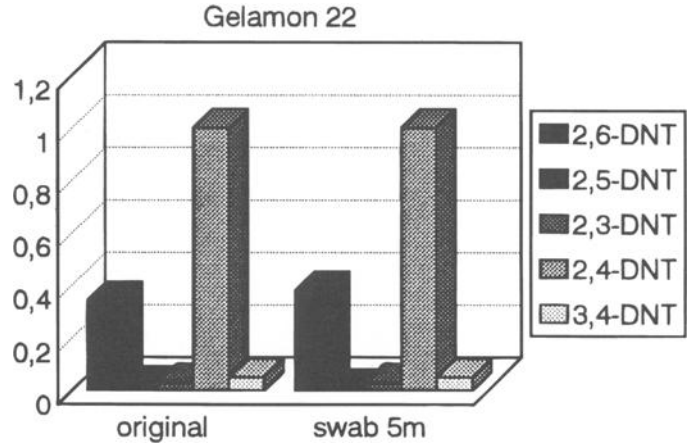
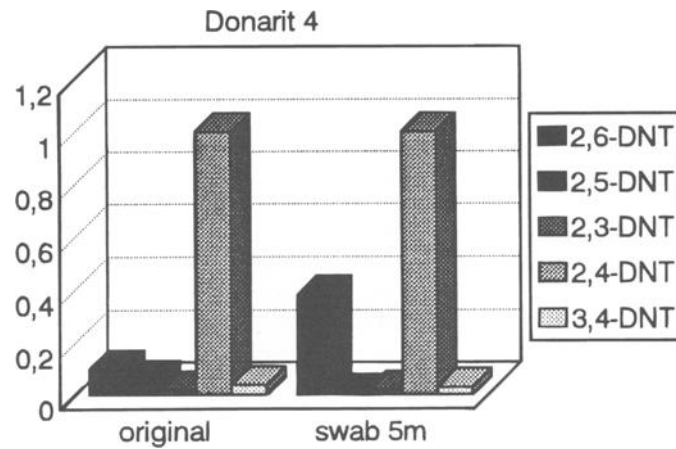
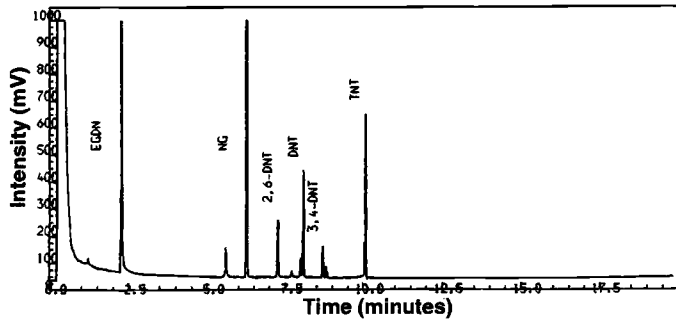
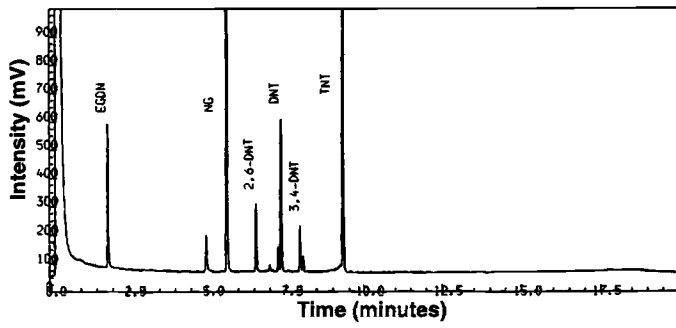


FIG. 4—Relative amounts of nitro-aromatics in post blast residue and original explosive.

FIG. 6—Relative amounts of nitro-aromatics in post blast residue and original explosive.

As mentioned in the sampling description, small particles from the original dynamite were found during the swabbing procedure, even at a distance of 10 m. The analysis of such a particle, which was one of the biggest, showed a very similar composition to the original. It is believed that most of the discussed results are based on the analysis of very small particles, visible and invisible, from the original explosive, which are collected during the sampling procedure. It was not possible to distinguish between explosive residue from the detonation process and small particles at the

TABLE 4—Ratio of components to 2,4-DNT.

	Geosit 3	1 m	2.5 m	5 m	5 m	5 m	7.5 m	10 m	10 m
EGDN	35.73	0.24	22.97	5.60	51.65	64.37	61.70	16.80	17.89
NG	0.54	0.06	0.09	0.53	0.45	0.45	0.59	0.27	0.04
2,6-DNT	0.27	0.24	0.32	0.25	0.01	0.56	0.29	0.25	0.20
2,5-DNT	0.11	0.06	0.05	0.14	—	—	0.01	—	—
2,3-DNT	0.42	0.16	0.09	0.40	—	0.01	0.01	0.26	0.06
2,4-DNT	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
3,4-DNT	0.81	0.28	0.16	0.71	0.01	0.01	0.38	0.39	0.14
TNT	1.15	0.67	0.87	0.91	0.55	0.14	1.46	0.84	0.13

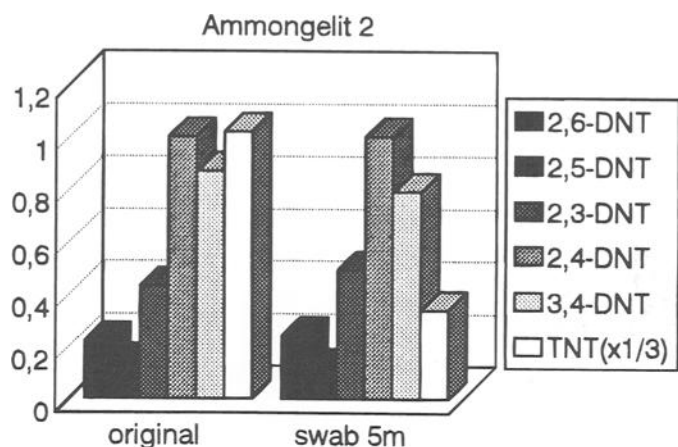


FIG. 7—Relative amounts of nitro-aromatics in post blast residue and original explosive.

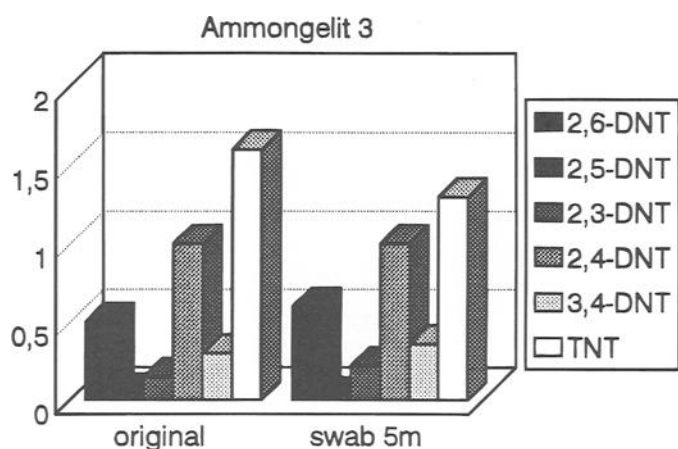


FIG. 8—Relative amounts of nitro-aromatics in post blast residue and original explosive.

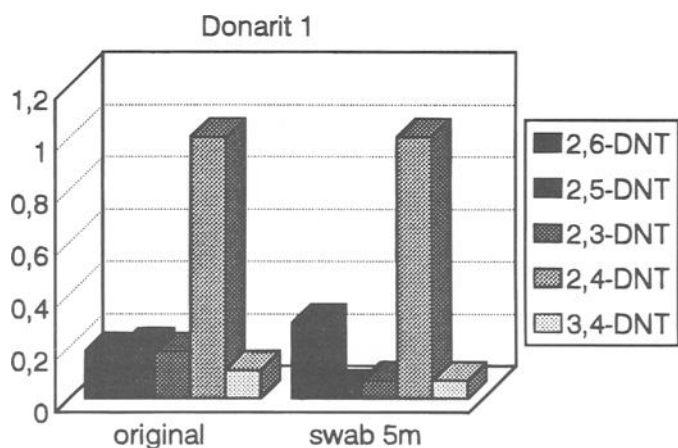


FIG. 9—Relative amounts of nitro-aromatics in post blast residue and original explosive.

detonation scene. The small particles are dispersed by the shock-wave if it reaches the border between the explosive charge and the free air. Because of their higher kinetic energy they fly farther than the micro droplets in the explosion gases. That effect explains the positive results finding residues from a 500 g charge on an area of 1 m² in 10 m distance.

Absolute Amounts of Explosive Residues

An often-asked question deals with the amount of explosives that can be found after the detonation. Because many parameters affect the distribution of residues (for example, the type and direction of the initiation, and the type of containment) only an approximate answer can be given. A simplified theoretical model and analytical results are presented in the following in an effort to help answer the question. With the experimental arrangement as described previously, it is also possible to analyze the total amount of explosive, that is found on an area of 1 m² at a given distance. If the explosive residue is deposited on the metal surface only from the blast, the absolute amount should rapidly decrease with increasing distance. From a theoretical view the explosion gases from the blast should be diluted with the third power of the distance. Apart from the pressure that decreases only squared with the distance, the extension of the explosion gases is not a shock-wave, it is spread in a ball. Because the explosion gases are collected on a surface perpendicular to the direction of extension the third power is reduced to a squaric dependency. So there are only two directions of diluting: the two axis of a ball shell. The diameter of the so called fireball (Fig. 11), the region where the unburned components of the explosive have enough concentration and heat to form a fire ball by the reaction with the oxygen from the air, can be calculated from the radius of the charge (R_0). Presuming that the density of air is 1200 to 1500 times smaller than the density of usual explosives, the radius of the fire ball (R_k) is calculated as [9]:

$$R_k = (1200)^{1/3} R_0 \text{ until } R_k = (1500)^{1/3} R_0$$

$$\text{or } R_k = 11 R_0 \text{ until } R_k = 12 R_0$$

This radius is of great importance for the explosion theory in air. After the gases of explosion have reached that radius R_k , the gases have displaced the corresponding amount of air and the extension of the gases is slowed down. The explosion gases have reached the form of a ball cloud and the further extension is slow. The higher evaporating gaseous components condense and form micro droplets. The concentration of explosive residues in the cloud is diluted with the third power of the distance.

The radius of the fire-ball in this paper can be calculated to be about 2 meters, so that at farther distances the amount of explosive residues from the explosion gases should decrease tremendously. The absolute amounts of explosive residues found in the swabs from 1 m distances are listed in Table 5. Obviously the amounts decrease with increasing distance, but no regularity could be found to provide for a means of calculation to predetermine the values. That observation has already been explained. The extension of explosion gases from the blast is not the only effect to spread explosive residues. The previously mentioned dispersion of small particles from the outer surface of the charge is the predominant effect for the contamination of surfaces at distances that are higher than that distance theoretically expected for the explosion gases.

Conclusion

In the post blast residue of dynamites, that contain nitro-aromatic compounds, the isomers of dinitrotoluene and/or trinitrotoluene can be detected. Using an analytical system with enough resolution efficiency to separate and quantify the different isomers, much information can be gathered to identify the explosive. The brand can be determined in comparison with a known sample of explosive or by search in a special data base. The best explosive residue for characterization after the detonation are unreacted microparticles

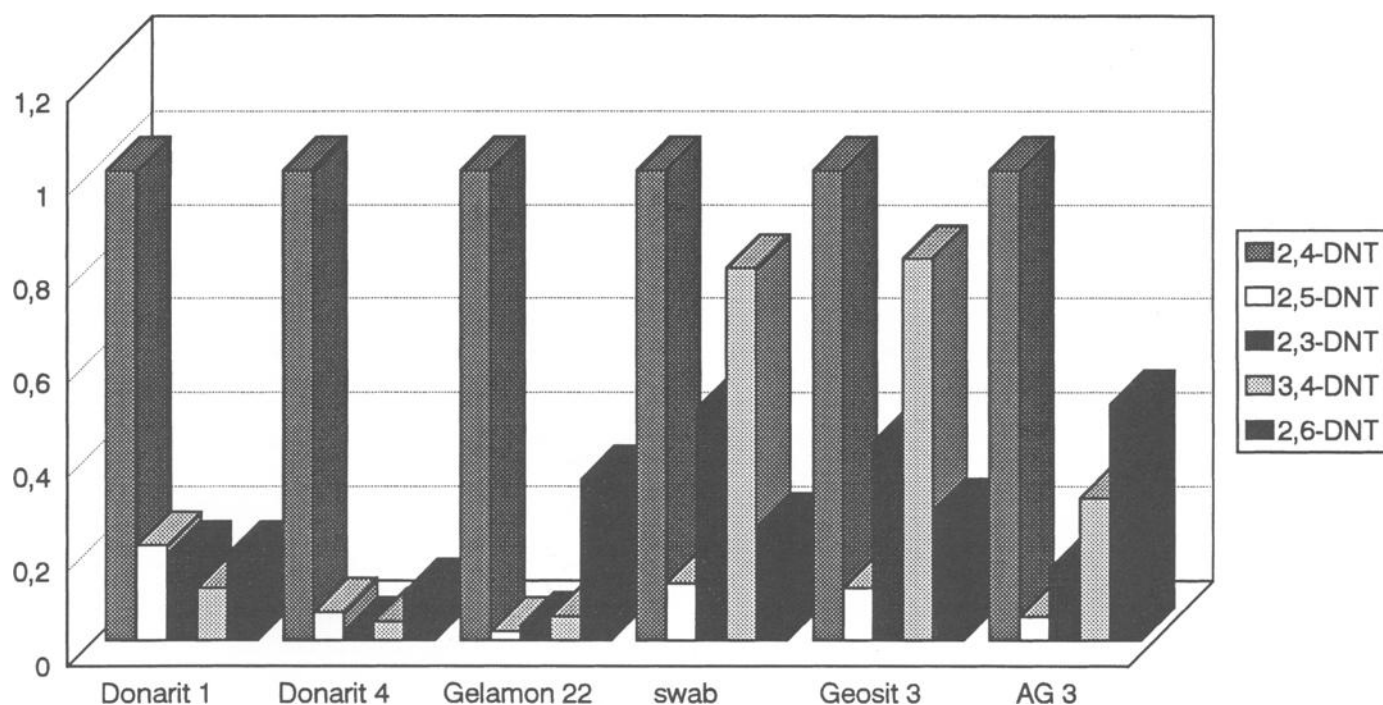


FIG. 10—Comparison of post blast residue with original explosives.

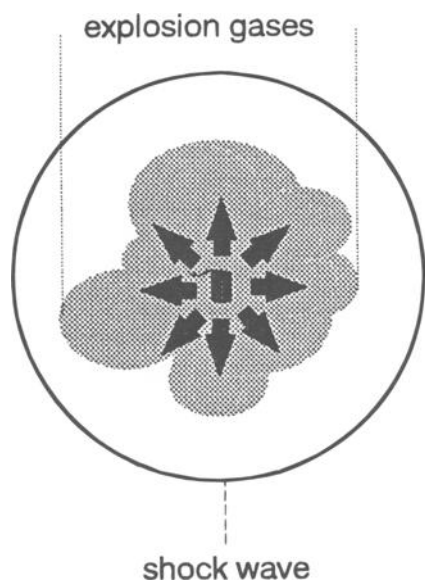


FIG. 11—Shock wave and explosion gases.

TABLE 5—Absolute amounts in different distances (µg).

Geosit 3	1 m	2.5 m	5 m	7.5 m	10 m
EGDN	7.80	185.62	10.40	8.04	6.72
NG	2.14	0.90	0.15	0.13	0.02
DNT	45.10	14.55	0.32	0.21	0.61
TNT	26.79	10.32	0.16	0.29	0.07

AG 2	1 m	2.5 m	5 m	7.5 m	10 m
EGDN	0.85	155.01	42.88	32.93	21.11
NG	47.20	50.03	0.86	4.90	4.80
DNT	72.60	32.97	1.25	1.94	2.74
TNT	184.57	143.21	0.46	6.93	6.56

from the original explosive, that are spread into the environment. If the explosive charge is uncovered and free hanging such micro-particles may be found up to several meters in distance from the center of the explosion.

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