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The Use of the Gandolfi Camera as a Screening and Confirmation Tool in the Analysis of Explosive Residues

In the past, bombing cases were relatively uncommon and evidence from these cases seldom found its way into the forensic science laboratory. Therefore, only a limited amount of research in the area of explosive residue analysis has been carried out. Today, however, according to the current figures from the National Bomb Data Center the reported incidence rate is about 5.8 bombs per day [1]. As S. G. Styles [2] remarks: "Terrorism is a fact of life today in all parts of the free world. It grows up in a climate of political, religious or doctrinal tensions; it erupts with violence, death and destruction." Rather than being a rarity, bomb residues are becoming a part of everyday forensic science laboratory analysis. Thus, the forensic science laboratory today is being frequently asked to determine if in fact a bombing has taken place or if some accident such as a natural gas leak caused gas to accumulate in the presence of an ignition source, resulting in an explosion. In addition, where the damage characteristic of a high explosive is noted, the capability of identifying the type of explosives used in a bombing would be helpful as an investigative aid in limiting the number of possible avenues to be pursued by investigators. It would be important to distinguish between explosions resulting from compounds such as picric acid or ammonium nitrate, which may have legitimate non-explosive uses and may have been detonated accidentally in storage, and those substances such as military explosives whose presence at the origin of an explosion would imply a purposeful design. Further subdivision of this latter group by use of definitive chemical identification schemes could aid in determining the source of supply and possibly the perpetrator.

Because of the present high rate of reported bombings combined with the importance of being able to identify the substance responsible for the explosion, it would appear that a simple, positive method for screening and identifying trace quantities of explosive residues is needed by forensic science laboratories. On reviewing the literature, one finds a number of papers and books on the subject of explosive analysis. However, most deal with a single specific class of explosive or method of analysis. As Pristera et al state in Ref 3, "There are no simple detailed methods for the qualitative analysis of unknown explosives except general methods of organic analysis."

Most of the earlier studies were generated by governmental agencies, such as Picatinny Arsenal, with macroscopic samples. Such large samples are rarely encountered in bomb

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debris; generally, microscopic samples are recovered. Therefore, many of the earlier studies are of limited value for use in the forensic science laboratory.

Instrumental techniques, including infrared (IR) spectroscopy and X-ray diffraction, have long been employed for the analysis of explosives. As early as 1947 the California Institute of Technology (CIT) demonstrated that X-ray diffraction patterns could be of considerable value for the rapid identification of many crystalline constituents found in explosives of unknown composition [4]. Personnel at CIT examined 18 organic compounds present in explosives, giving interplanar (*d* values) spacings and approximate intensities for these compounds. Infrared spectroscopy has also been very effective in identifying explosives where relatively large samples are available [5]. In 1960 Pristera et al [3] released a paper giving 68 IR spectrograms covering all common high explosive ingredients, additives, and related compounds. The primary limitation of this paper from the forensic science point of view is that macroscopic samples were used. However, this paper is useful as a reference if sample size and purity permit the use of IR spectroscopy. A large number of additional IR spectra and data on X-ray interplanar spacings for the identification of explosive materials are located in Ref 6.

In contrast with the history of methods primarily designed for dealing with undetonated explosives, research into the analysis of explosive residues was cursory and sporadic until 1970 when Jenkins and Yallop [7] published what could be considered the most useful research done in this field until very recently. They investigated the use of thin-layer chromatography (TLC) in the analysis of explosive residues. Their work proved that small traces of military explosives could be detected on steel plates 60 cm from the center of an explosion. Furthermore, they found nitroglycerine could be detected even after a 1-year period. It is important to note the use of the word "detect" and not the word "identify" in the previous statement. Although TLC is an excellent tool for screening, it cannot be considered a positive means of identification [8].

Early in 1974 Doali and Juhasz [9] investigated the use of high-speed liquid chromatography (HSLC) in the qualitative and quantitative analysis of compounds found in propellants and explosives. They found it possible to separate mixtures of closely related compounds such as toluene; *p*-nitrotoluene; 2,4-dinitrotoluene; and 2,4,6-trinitrotoluene (TNT) in less than 15 min. This rapid separation and attendant purification could be useful in the forensic science laboratory for the analysis of bomb residues. The above researchers also reported separating and quantitating explosives such as TNT, tetryl, cyclotrimethylenetrinitramine (RDX), nitroglycerin, and cyclotetramethylenetrinitramine (HMX), as well as other compounds commonly found in residues, such as diphenylamine and dibutyl phthalate. From their research they concluded that HSLC is "a simple and rapid method for the analysis of typical explosives and propellants" [9].

Researchers at Waters Associates, a liquid chromatography equipment supplier, have been carrying out some work in the field of explosive analysis using HSLC.³ In a recent communication they reported separating RDX and pentaerythritol tetranitrate (PETN). In addition, they have examined ball powder and isolated nitrocellulose, diphenylamine, dinitrotoluene, and TNT. The encouraging results to date with HSLC suggest that further research is warranted. It is especially important to learn whether this technique can be applied to the residues from actual cases where the samples available for analysis are severely limited. A further difficulty with HSLC is that, like TLC and other chromatographic techniques, it cannot be considered a positive means of identification. This limitation does not preclude the possibility of HSLC being very useful when used in conjunction with other techniques.

Recently Beveridge et al [8] found that X-ray diffraction and IR are "prime identifica-

³Waters Associates, Inc., Milford, Mass., personal communication, 1975.

tion techniques." In this work they used IR as an identification tool for carbonates and nitrates commonly found in bomb residues. However, they found it difficult to obtain identifiable X-ray diffraction powder patterns and IR spectral patterns when sampling actual explosive residues employing solvent extraction because the solvent extract often contained contaminants, most commonly "calcium sulfate from building products, ammonium chloride from batteries, sodium chloride of unknown origin and resins" [8].

From the above discussion it can be seen that an ideal technique would have to be both sensitive and definitive and, in addition, should be able to deal with the contamination problem encountered with actual explosive residue samples. This ideal is closely approached for crystalline residues by the Gandolfi camera, which is capable of producing a detailed X-ray diffraction pattern for a single microscopic crystal [10]. Further, X-ray diffraction patterns are generally conceded to be quite distinctive for a given crystalline compound, and the patterns obtained with the Gandolfi camera are directly comparable with the results of powder diffraction studies. Thus, it would appear that, with regard to the positiveness of identification and to the sample size or sensitivity needs, the Gandolfi technique is well suited to explosive residue analysis. Contamination difficulties can be eliminated if the requisite intact microscopic crystals can be found in the residue. Locating, mechanically removing, and identifying these crystals eliminates the need for a preliminary solvent extraction with its attendant contamination problem.

Picatunny Arsenal recently released a report [1] on the use of computers in identifying explosive mixtures by X-ray diffraction. In this report [for which data were supplied by one of the present authors (D.V.C.)] a brief study of the capabilities of the Gandolfi camera has indicated its potential use in the forensic science laboratory for the identification of explosives in small quantities, "often in the form of small fragments of a single crystal" [11]. It was also pointed out in this report that the Debye-Scherrer powder camera yields diffraction patterns from samples weighing between 10 and 15 mg (a rather high figure in our experience, although losses during grinding and sample preparation often necessitate an initial sample significantly larger than that which is actually placed in the camera), whereas "the recently available Gandolfi camera allows the production of diffraction patterns from single crystals as small as 30 microns" in diameter [11]. The mass of a cubic particle this size with an assumed density of one would be roughly 30 ng (≈ 15 ng if spherical). Thus, if we assume an approximate 1-mg sample size for the Debye-Scherrer camera, we see that the Gandolfi camera is capable of analyzing a sample more than four orders of magnitude smaller than that needed for analysis by the classical powder camera method.

Theory

The Gandolfi camera is in many respects similar to the more familiar Debye-Scherrer powder camera described in physical chemistry texts. The Gandolfi camera is available in two standard diameters (57.3 mm and 114.6 mm), as is the case with the most commonly used Debye-Scherrer models, and will accept film which has been cut to these standard sizes. These standard diameters are selected so that the position of a line on the film in millimetres will be an integral multiple (1 or 2) of its corresponding 2θ Bragg diffraction angle. This is measured from the film position for the undeviated beam.

The interpretation of the diffraction pattern on the film is the same for both the Gandolfi and Debye-Scherrer cameras. The main differences between the two designs concern the type of sample and the manner in which it is mounted and rotated in the X-ray beam. The Debye-Scherrer system insures the presentation of all possible crystal orientations to the X-ray beam by using numerous small crystals randomly oriented and by rotating the sample concentrically with the cylindrical axis of the camera. The Gandolfi

system uses a single small crystal which is rotated through essentially all orientations through the use of a double rotary motion. The sample is mounted on the end of a shaft which makes an angle of 45 deg with respect to the cylindrical axis of the camera. By a simple gearing arrangement the shaft is rotated on its own axis while this axis is made to describe a conical surface which has the sample locus as its apex (Fig. 1).

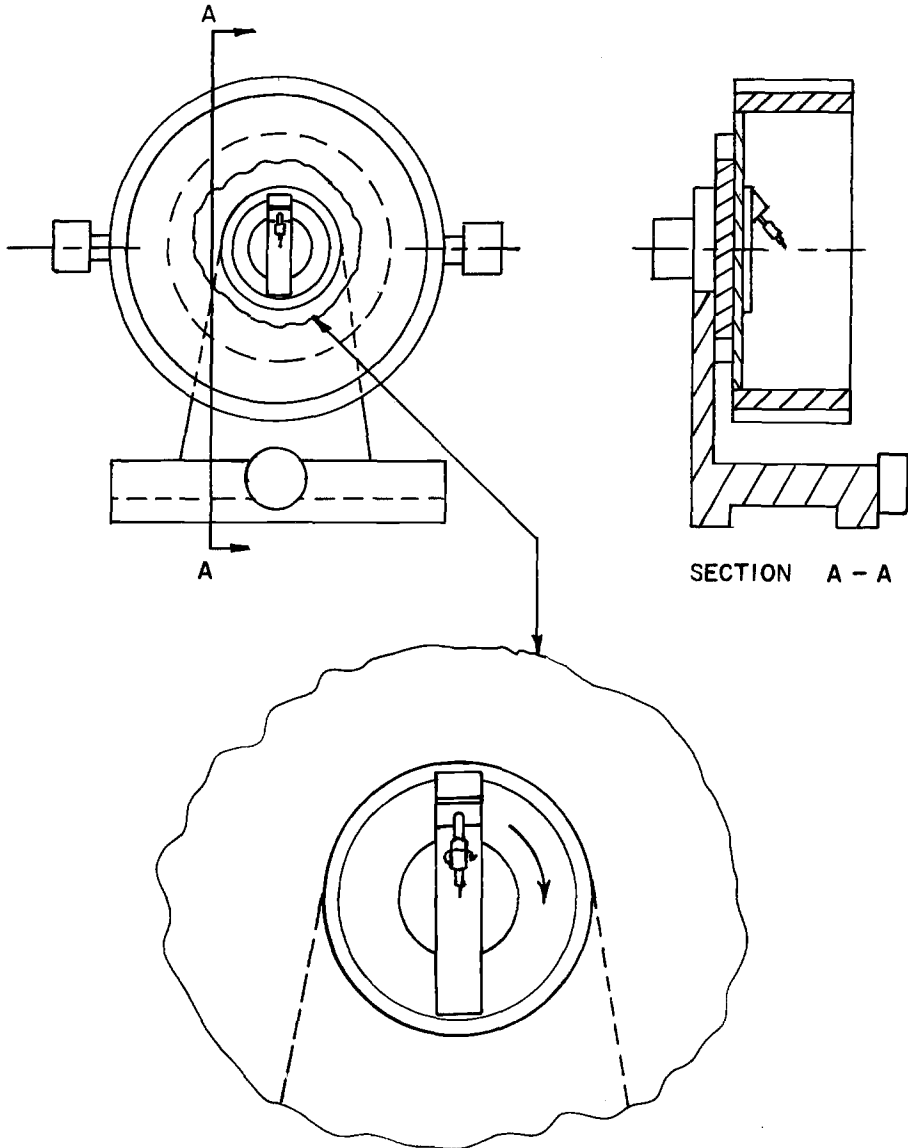


FIG. 1—Diagram of two views of the Gandolfi camera with an enlarged inset showing the sample mounting area.

Methods and Materials

The known explosives used in this study were from a collection maintained by the

New Jersey State Police Laboratory, Little Falls, N.J. The samples from unknown and test explosions were mechanically removed from the residue with the aid of low power magnification and prepared sample mounting rods. The sample mounting rods consisted of 0.1 to 0.3-mm diameter glass rods whose tips were dipped in office-type rubber cement just prior to use. The use of rods smaller than 0.1 mm is preferred because it results in less fogging of the film because of scattering of the X-rays during long exposures. The diameter of the rod should be less than that of the crystal. The desired crystal was sampled by contacting it with the tip of one of these rods. When actual case samples were being examined, the residue was first searched for particles and fragments of such things as wires and blasting caps. These were studied for possible clues as to what type of device was employed.

The crystal fragments that were selected for analysis using the Gandolfi camera were inspected with a stereomicroscope to be certain that they were free of adhering surface impurities. The rod and crystal assembly was then mounted in the camera and aligned according to the manufacturer's instructions [1]. The Gandolfi camera (Catalog No. D1100) was obtained from Blake Industries, Inc., Springfield, N.J. This model can also be used as a conventional Debye-Scherrer powder camera. A photograph of the Gandolfi camera is presented in Fig. 2.

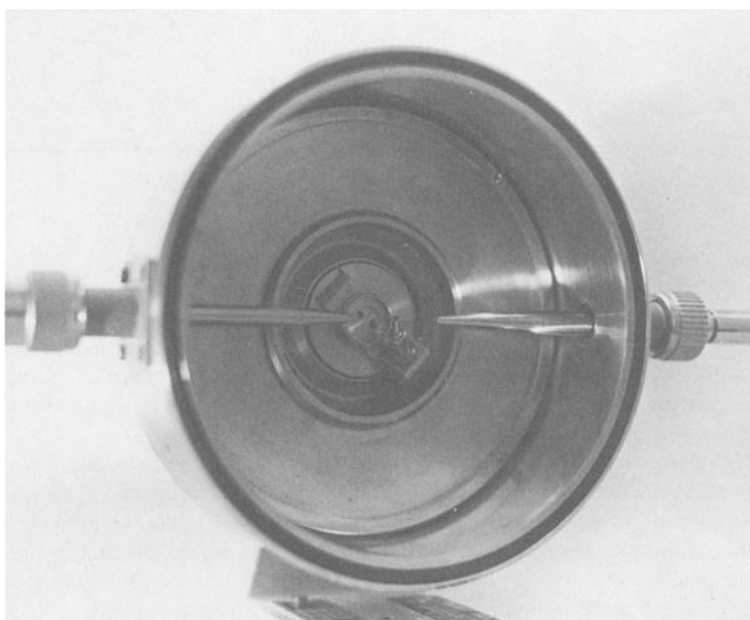


FIG. 2—The Gandolfi camera with the cover removed.

The operating conditions of the X-ray generator were kept constant at 40 kV and 20 mA. The X-rays were produced from a copper source and filtered with a nickel filter to remove K_{β} radiation. The characteristic radiation obtained under these conditions is

$K_{\alpha(1, 2)}$. The weighted average for the wavelength is 0.15418 nm. All 2θ angles were read with a Norelco film reader, which could be interpreted to ± 0.05 deg. No corrections were made for film shrinkage or temperature; however, it is interesting to note that all the d values recorded corresponded well with those reported in the literature (Table 1). Being able to read the film directly without making prior corrections will facilitate rapid interpretation of results by the practicing forensic chemist.

TABLE 1—Comparisons of the interplanar spacings obtained with the Gandolfi camera and the Debye-Scherrer powder camera. Interplanar spacings are listed in order by highest intensity.

TNT			PETN		
Gandolfi Camera	Powder Camera	Ref 6	Gandolfi Camera	Powder Camera	Ref 6
3.87	3.86	3.84	3.84	3.84	3.83
7.03	7.03	6.99	3.55	3.56	3.54
4.28	4.28	4.26	3.32	3.32	3.31
3.06	3.05	3.04	3.17	3.15	3.15
5.66	5.66	5.62	2.63	2.60	2.60
5.00	5.00	4.99	2.36	2.35	2.35
2.99	3.01	3.00	2.22	2.22	2.22
2.74	2.74	2.73	2.04	2.05	2.05
2.68	2.67	2.67	...	6.62	6.64
3.54	3.53	3.52	4.66	4.70	4.67
3.45	3.44	3.43	2.97	2.96	2.95
3.27	3.26	3.26	2.84	2.86	2.82
2.88	2.88	2.86	2.72	2.73	2.70

Results

The unknowns that were run were identified by comparing their diffraction patterns with those obtained for known samples and also by comparing these data with published interplanar spacings derived from powder diffraction studies. The correspondence between the published powder diffraction data and the data obtained from knowns using the Gandolfi camera was good. In rare cases it was found necessary to dismount the crystal fragment halfway through a run, turn it 90 deg, remount it, and continue the run to obtain the best diffraction pattern.

Samples of the explosive compounds and formulations listed in Table 2 were run on both the Debye-Scherrer and Gandolfi X-ray diffraction cameras. The information derived from a given explosive substance was essentially the same for either method, although the sample size necessary for the Gandolfi camera was as much as three orders of magnitude smaller. The degree of similarity for the data obtained by each method can be readily seen from an examination of Fig. 3. In this figure the diffraction patterns characteristic of TNT obtained by using both the powder camera and Gandolfi methods are presented.

Figure 4c shows the Gandolfi camera diffraction pattern obtained from a single crystal fragment found in the residue submitted in an actual explosives investigation. This fragment was easily identifiable by its characteristic diffraction pattern. This same case was examined earlier by extracting the sample with water and running it with a Debye-Scherrer powder camera to obtain a diffraction pattern. As can be seen in Fig. 4a, this pattern is not readily identifiable because of the presence of extra lines, whereas the fragment run with the Gandolfi camera is comparable in essential respects with the known control diffraction pattern shown in Fig. 4b.

TABLE 2—*Interplanar spacings for substances examined with both the Gandolfi camera and Debye-Scherrer camera in order of greatest intensity.*

Explosive	Interplanar Spacings															
	3.46	5.38	2.29	2.64	2.58	2.69	1.96	1.88	3.09	2.92	...	2.95	...	2.82
Silver fulminate ^a	3.83	3.54	3.31	3.15	2.60	2.35	2.21	2.05	6.64	4.67	...	2.70	...	1.81
PETN	3.04	6.75	5.10	4.95	4.35	4.02	3.50	3.30	2.76	5.72	2.56	2.36	...	5.34
RDX	2.81	4.31	3.86	3.28	6.02	3.02	5.53	3.42	2.42	4.03	4.84	2.95	...	2.18
HMX ^a	7.00	4.68	14.5	4.41	3.77	3.26	2.97	2.52	2.40	3.65	4.15	3.14	...	2.62
Tetryl	3.84	6.99	4.26	3.04	5.62	4.99	3.00	2.73	2.67	3.52	3.43	2.86	...	2.43
TNT	3.03	2.31	1.90	2.81	2.53	2.12	1.88	3.89	1.95	1.65	1.63	1.46	...	1.17
NaN ₃	3.45	3.34	2.87	2.79	2.78	2.33	2.12	4.41	2.15	2.14	4.29	1.92	...	6.69
KClO ₃	3.08	2.72	3.96	4.95	2.26	2.88	2.49	2.38	1.57	1.63	1.98	1.73	...	3.66
NH ₄ NO ₃																

^a Authors' collection. All other spacings are from Ref 6 or Joint Committee on Powder Diffraction standards data.

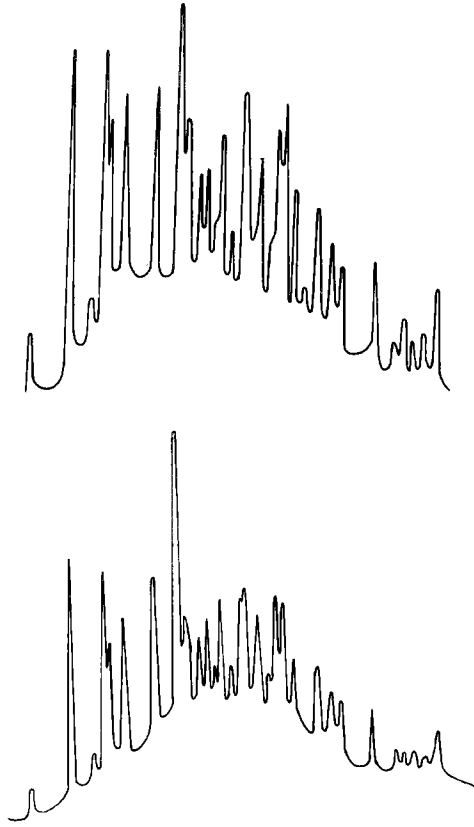


FIG. 3—Densitometric traces of X-ray diffraction films of TNT obtained with (top) the Gandolfi camera (sample size $\cong 1 \mu\text{g}$) and (bottom) the Debye-Scherrer powder camera (sample size $> 1 \text{mg}$).

Discussion and Conclusions

The results obtained using the Gandolfi camera with single grains of explosives clearly show it to be a valuable means for analyzing and identifying explosive residues found at the scenes of bombings. This technique has numerous advantages over many of the methods that are currently used. It can produce a definitive identification for small residue particles based on data already available in X-ray diffraction files. In addition, it is nondestructive and can be easily integrated into an overall scheme for the identification of explosive residues. Such a scheme would differ significantly from those currently used. Swabbing or solvent extraction, for example, would not be employed, at least until the surfaces suspected of containing residue had been thoroughly inspected with a stereomicroscope and all bomb fragments and potentially useful crystalline particles had been removed from the residue. In some cases it might be advisable to refrain from extracting the remaining residue from the surface until the results of the X-ray diffraction analyses of the crystalline residue particles are interpreted. If these results produce an identification of the explosive, this may eliminate the need for any further analytical work. However, the particles identified may merely be those of a substance or substances often associated with particular explosives or explosive devices. In such an instance this information would suggest leads for further investigative and testing procedures. This might help in selecting the best solvent to be used for the extraction of the remainder of the residue.

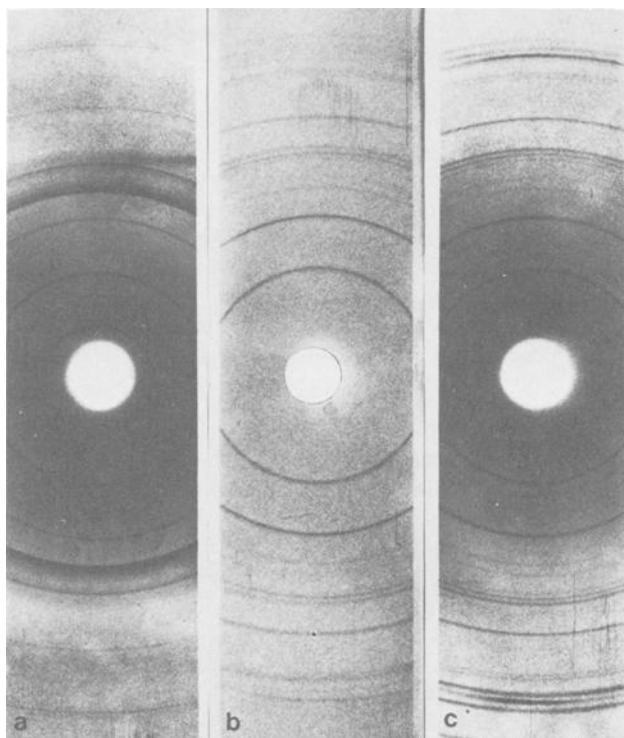


FIG. 4—X-ray diffraction patterns obtained during the investigation of an explosives case submitted to the Little Falls Laboratory of the New Jersey State Police. See text for a full explanation of this figure. The unknown was identified as silver fulminate with the Gandolfi camera. (a) Water extract, powder camera; (b) known control; and (c) unknown, Gandolfi camera.

If no crystallographically identifiable particles are found, more reliance must be placed on the results of the examination of the scene. The visual and stereomicroscopic examinations, although always important, assume additional importance in such circumstances. In addition to particles of explosives a careful inspection will often reveal the presence of particles and fragments of blasting caps, wires, batteries, and other devices which may be very useful in mentally reconstructing the explosive device. Such information will frequently be of great help in deciding which type of explosive compound to expect in the residue. If an extraction is necessary, a more informed choice of solvents can then be made.

A general procedure for explosive residue analysis and identification should have an investigative approach rather than a straight chemical one. For this reason the need for the preliminary visual and microscopic inspection discussed above cannot be over-emphasized. If a solvent extraction by swabbing were employed prematurely, valuable information could be lost. The distribution and physical integrity of the particles would be destroyed by the solvent and, in addition, environmental impurities could be dissolved and incorporated into the extract, greatly complicating any subsequent analysis. The Gandolfi camera is ideally suited for use in such an investigative scheme since it can deal with individual particles in the residue which have been selectively removed without altering either the particles or the remaining residue. It may be argued that the painstaking inspection and selection of individual particles from the residue which is necessary to obtain samples for the Gandolfi camera is too time-consuming. It must be remembered,

however, that this thorough visual and microscopic inspection should be part of any residue analysis scheme no matter what analytical method is to be employed for identification [12]. While a search is being conducted for fragments of primers, wires, and other debris, it is a simple matter to select candidate particles for subsequent analysis by the Gandolfi camera.

The general steps of a recommended scheme for use with the Gandolfi camera are summarized below. A more detailed scheme is presented in the thesis on which the present paper is based. This scheme assumes that the criminalist or investigator is familiar with the principles of bomb scene investigation and has had some experience at bomb scenes. It also assumes that the scene has been thoroughly searched and that the articles that are to be removed to the laboratory for analysis will be handled with care so that loosely held particles are not brushed or knocked free. The steps are as follows:

- (1) thorough visual and microscopic inspection of promising fragments and surfaces from the vicinity of the origin of the explosion;
- (2) a tentative mental reconstruction of the explosion and the explosive device;
- (3) removal of candidate crystalline fragments for analysis by the Gandolfi camera;
- (4) analysis with the Gandolfi camera of crystalline particles removed from the residue;
- (5) interpretation of the Gandolfi results;
- (6) modification of the mental reconstruction as necessary in light of the Gandolfi results;
- (7) a decision as to whether a solvent extraction is now appropriate or whether the information gleaned thus far is sufficient to allow the case to be reported; and
- (8) if a solvent extraction is deemed necessary, selection of solvent and subsequent analytical procedure based on what has been learned in the foregoing steps.

Summary

A method for analyzing and identifying a single crystal of explosive as small as 30 μm in diameter in an explosive residue has been described. The method uses the Gandolfi X-ray diffraction camera to produce a detailed X-ray diffraction pattern for this small crystal which is directly comparable with the data obtained by powder diffraction methods. The role of this technique in an overall scheme for explosive residue analysis was also discussed. The need to use an investigative as opposed to a chemical approach was emphasized.

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