

## Post-blast detection of traces of explosives by means of Fourier transform infrared spectroscopy

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### ABSTRACT

Samples obtained from debris after explosions of about 30 g of energetic materials were analyzed by means of Fourier transform infrared (FTIR) spectroscopy using both, Global and synchrotron infrared radiation at the ISMI beamline of the Singapore synchrotron light source (SSLS). Low- and high-strength-of-explosion blasts were performed during each test run with the same explosive material. From the spectroscopic measurements, traces of unreacted explosives were found on more than 200 different materials that served as sample catchers in the explosions.

The integrality of the experiments done confirmed that FTIR spectroscopy is a sufficiently sensitive method to detect traces of explosives in post-blast residues even of high-strength explosions. The method requires only a minimal amount of sample and enables accurate and very fast identification of the presence of explosive material. Finally, the synchrotron radiation infrared source provided one order of magnitude higher sensitivity compared to the conventional Global source.

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## 1. Introduction

Increasing the capabilities and efficiency of forensics teams, police forces, and homeland security in sensing potentially hazardous materials is of prime concern to governments. The growing threat and sophisticated criminal activities committed using energetic materials in recent years have generated the need for fast and accurate investigation techniques for evaluating vital clues left at the crime scene. The post-blast analysis of trace amounts of explosives is particularly difficult because traces are usually trapped in or deposited on various debris materials. Identifying unknown explosives requires the ability to quantitatively determine a large number of inorganic and organic materials. While there is a great deal of published literature describing methods for the analysis of organic explosives by various methods, there are comparatively few publications concerning the analysis of explosives based on post-blast residues. Analysis of post-blast residues is very important, enabling the scientists to identify the explosives that were used in the blast, eventually helping to find hints to their likely origin. There are

many difficulties involved in the identification of explosive materials and devices after an explosion including the scanty amount of substances that is left, the reaction of some products of disintegration with the surface of other materials, and the fact that mostly gaseous final products are generated like water and carbon oxides which are not very characteristic analytically.

Usually, the analysis of post-blast residues begins with a number of colorimetric screening tests (alcoholic KOH, Griess reagent, diphenylamine, etc.) [1–3]. These tests are quite rapid, but, unfortunately, very often not definitive. Different methods [1–14], some of which are presented in Table 1, can be used to analyze post-blast residues. These techniques are quite sensitive, but generally involve time-consuming processes requiring special and complex sample preparation which leads, as a main drawback, to the possible destruction of the samples examined.

Apart from the above-mentioned disadvantages of methods which are involved in post-blast residues analyses, one persistent problem for the forensic group in analyzing them is the lack of extensive knowledge about what may be present in the residues. Current knowledge of chemical makeup of explosive residues generally comes from actual criminal casework. Crime scenes where explosions have occurred are particularly challenging to process, due to their complexity – the detonation not only consumes most of the explosive material, but also produces a

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**Table 1**

Advantages, limitations and the sensitivity range of various techniques used for the detection of the explosives [1–14].

| Analytical method                                              | Abbreviation | Target explosives     | MDL      | Advantages                                                              | Limitations                                                 |
|----------------------------------------------------------------|--------------|-----------------------|----------|-------------------------------------------------------------------------|-------------------------------------------------------------|
| Ion chromatography                                             | IC           | Inorganic             | ppb      | Reliable identification                                                 | Limited to inorganic ions                                   |
| Ion mobility spectrometry                                      | IMS          | Organic and inorganic | ng       | Simple, quite sensitive                                                 | The molecules of the sample need to be ionized              |
| Thin layer chromatography                                      | TLC          | Organic               | μg       | Simple, inexpensive, rapid                                              | Low resolution susceptible to contamination                 |
| Gas chromatography-electron capture detector                   | GC-ECD       | Nitrogen containing   | pg       | Rapid, selective, highly sensitive                                      | Requires volatile analytes insensitive to hydrocarbons      |
| Gas chromatography-thermal energy analyzer                     | GC-TEA       | Organic               | ng       | Sensitive                                                               | Low selectivity                                             |
| High-performance liquid chromatography                         | HPLC         | Organic and inorganic | pg       | Universal (organic and inorganic compounds have characteristic spectra) |                                                             |
| Fourier transform infrared spectroscopy                        | FTIR         |                       |          |                                                                         |                                                             |
| Mass spectrometry                                              | MS           | Organic and inorganic | pg to ng | Selective, sensitive                                                    |                                                             |
| Gas chromatography-mass spectrometry                           | GC-MS        | Organic               | pg to ng | Selective, sensitive                                                    | Limited to volatiles                                        |
| Scanning electron microscopy/energy dispersive X-ray detection | SEM/EDAX     | Organic and inorganic | pg to ng |                                                                         | Expensive, limited to inorganic molecules of the explosives |

complex mixture of interfering compounds. Post-detonation explosive compounds are difficult to detect and analyze because their trace amounts are spread over a large debris field.

In order to gain reliable information about post-blast residues, we mostly worked on samples originating from the explosions made on purpose to create these remnants. The aim of this study was also to demonstrate, for the first time, that synchrotron-radiation-based FTIR spectroscopy is a particularly selective and sensitive method for the analysis of traces of explosives in post-blast residues. FTIR spectroscopy is certainly one of the most important analytical techniques available to date [15,16] and has been successfully used to analyze pure explosive materials in many laboratories worldwide [17,18]. However, to our knowledge, this method has not been applied to the analysis of post-blast residues [14].

## 2. Experimental

### 2.1. High explosives background

The energetic materials used in this investigation are C-4, PETN, TNT, and RDX. C-4 (composition C-4) is a plastic explosive in which the explosive agent is RDX. Trade names of RDX are Cyclonite or Hexogen, the IUPAC name is 1,3,5-trinitro-1,3,5-triazinane. C-4 is composed of 91% by weight of RDX with the remainder composed of plasticizer and a few percent binder. A major advantage of C-4 is that it can be molded into any desired shape. RDX is a white crystalline powder that is found in a large number of military explosive compositions and is considered to be one of the most stable and powerful high explosives. RDX' molecular structure is shown in Fig. 1a. It consists of an unusual six-membered

heterocyclic ring comprising three nitrogen and three methylene groups, with a nitrite group attached to each of the nitrogen atoms in the ring. This high nitrogen and oxygen content contributes to making RDX an excellent explosive material. RDX belongs to the nitramine compounds.

PETN (pentaerythritol tetranitrate, IUPAC name: 3-nitrooxy-2,2-bis(nitrooxymethyl)propyl nitrate) is another well-known high explosive. It belongs to the nitrate ester compounds; its structure (Fig. 1b) features a carbon atom in the center with its usual four bonds extending out towards the corners of a tetrahedron. Each of these four bonds connects to a methylene group which is another carbon attached to two hydrogens ( $-\text{CH}_2-$ ). Each of these carbons has one free bond sticking out to attach a nitrate group ( $-\text{NO}_3$ ). Upon ignition, the oxygen atoms in the nitrate sub-group terminals oxidize the carbon and hydrogen in the interior.

TNT (2,4,6-trinitrotoluene, IUPAC name: 2-methyl-1,3,5-trinitrobenzene) is a yellow, odorless solid, the structure of which is shown in Fig. 1c. It belongs to the nitroaromatic compounds. TNT has a number of specific properties that make it a nearly ideal explosive for military applications. It is relatively stable and has low sensitivity to impact and friction with respect to undesired detonation. Easy to store and handle, it has a high detonation power. When reacting, TNT molecules disintegrate. The oxygen atoms combine with carbon and hydrogen atoms, making carbon monoxide and water. The nitrogen atoms are freed and nitrogen gas is released. This transformation from a compact solid to a cloud of gas produces an enormous pressure and a powerful explosion.

All three explosives are characterized by high velocities of detonation and have applications in detonators, boosting charges

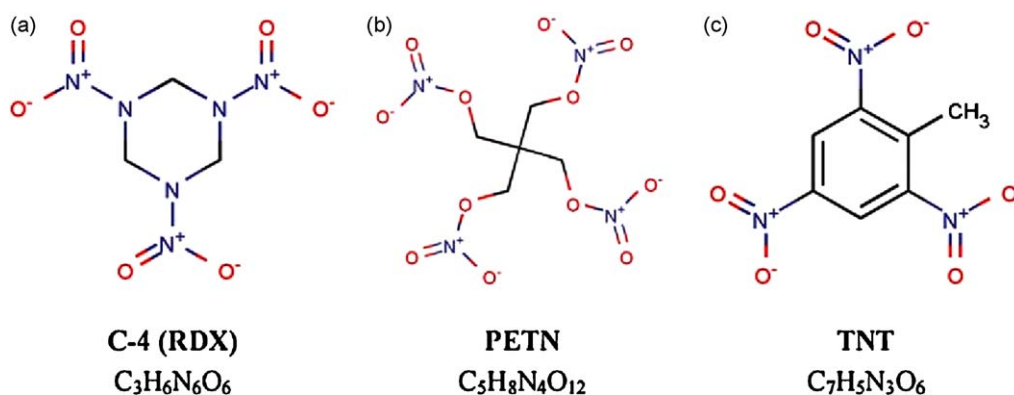
**Fig. 1.** Chemical structures of (a) C-4, (b) PETN and (c) TNT.

**Table 2**

Detonation parameters of explosives [12].

| Name of explosive | Density [g/cm <sup>3</sup> ] | Detonation velocity [m/s] | Detonation pressure [GPa] | R.E. factor <sup>a</sup> | Heat of detonation [MJ/kg] |
|-------------------|------------------------------|---------------------------|---------------------------|--------------------------|----------------------------|
| C-4 (RDX)         | 1.63 (1.77)                  | 8092 (8700)               | 25.7 (33.8)               | 1.34 (1.60)              | 6.61 (4.54)                |
| PETN              | 1.67                         | 8000                      | 30.0                      | 1.66                     | 6.15                       |
| TNT               | 1.64                         | 6930                      | 21.0                      | 1.00                     | 4.23                       |

<sup>a</sup> Relative effectiveness factor (R.E. factor) is a measure of an explosive's power for military demolition purposes. It is used to compare the effectiveness of an explosive relative to TNT by weight only.

and military ordnance [19]. Although high explosives are used to initiate and boost low explosives, they are totally consumed in the ensuing reaction and leave little traces for the forensic chemists to find. Most explosive materials are not used in their pure molecular crystalline form, but are mixed with other agents to make plastic explosives. The range and relative concentration of these mixtures vary from sample to sample, although the explosive compounds generally dominate the composition.

Table 2 presents the most important detonation parameters of explosives considered in this paper [20]. The detonation velocity is the rate at which the detonation shock wave proceeds through an explosive charge. It can be expressed as a function of basic parameters, namely the elemental composition, oxygen balance, initial density of explosive material [21]. The detonation pressure (Chapman–Jouguet pressure) is the pressure produced at the reaction front of the detonation and is often calculated as a function of the heat of detonation, the number of moles of gaseous products of detonation per gram of explosive, the average molecular weight of gaseous products and the initial density of explosive material [22,23]. The heat of detonation is defined as the amount of energy released when an energetic material decomposes by exploding or detonating [22].

## 2.2. Sample catchers

In order to mimic the situation at a real explosion site, a great variety of little devices taken from daily life objects were prepared as “sample catchers” that were attached to the walls of a steel cage made from perforated sheet metal for ease of fastening sample catchers and to reduce its resistance to the detonation wave. The size of the steel cage was about  $16 \times 16 \times 15 \text{ cm}^3$ . Objects such as aluminum plates, aluminum boxes with holes, cardboards, plastic covers, paper, spoons made of soft and hard plastic, towels, fabrics, copper tubes, pieces of hoses, plastic plates, wooden plates, were fixed to the four walls of the cage. Fig. 2a shows a photograph of the assembled steel cage. The catchers were to provide a more effective and faster collection of residues after explosion and to maximize the number of materials collected for further analysis.

## 2.3. Test explosions

Controlled explosions were performed at the facility of Advanced Material Engineering (AME) Pte Ltd., Singapore.

C-4, PETN, and TNT (amount <30 g) were detonated in separate test runs in a small steel container (volume  $18 \times 18 \times 18 \text{ cm}^3$ ,

thickness of walls 1.5 cm) dedicated to experimental tests of small amounts of explosives (property of AME Pte Ltd.). The explosive material and the sample cage with catchers were put in the steel container (Fig. 2a). The detonations were carried out by experts from AME Pte Ltd. Before each blast, the container with the explosive and sample catchers was surrounded by sand bags.

Two kinds of blasts, low- and high-strength, were performed with each explosive. The terms low- and high-strength explosion describe the efficiency of a particular explosion. A high-strength detonation is characterized by the rapid combustion of explosive materials, a rapid expansion of the resultant gases, and a build-up of high heat and pressure. In this case, the reaction propagates through the reacted material towards the unreacted material at a supersonic velocity as a shock wave. The detonation velocity of this reaction ranges from 2000 to 8000 m/s depending on the type of explosive material (Table 2).

In a low-strength detonation, the consumption of the explosive is less than 100% and it is typically characterized by increased burn time and light intensity, reduced blast pressure and momentum, and the presence of unreacted residual explosive. Reasons for an incomplete initiation of the material may be numerous including old or deteriorated explosives, poor contact between the explosive and the initiator, an insufficient initiator for the type of explosive being used and premature failure of the containing device [24–26].

In our case, the low-strength explosions were purposely created through the attenuation of the detonation shockwave from the non-electric detonator, lead azide mesh, used in the trials. The obstructed shockwave from the detonator would not be sufficient to further propagate through the explosive charge, resulting in an incomplete detonation. In the technical terms ammunitions, this is known as a failure in the explosive train.

After all low-strength explosions, all catchers remained in the container, partly featuring macroscopic traces of explosive material on their surfaces. Fig. 2b shows a photo taken after the blast with PETN for a low-strength explosion.

Even after high-strength explosions, many of the sample catchers were found inside the container as shown in Fig. 2c. This fact obviously increased the number of samples for further analysis and increased the chance of finding the traces of explosive materials embedded in different materials after completed explosions.

To compare the effect of our test explosion of about 30 g of high explosive with a real scale explosion such as the one that occurred in the Bali bombing attack where 5 kg of TNT were used, we calculate the “scaled distance” [20,27] that is defined as the distance at which the same effect in terms of peak overpressure of the blast wave is



**Fig. 2.** Container with sample catchers (a) before controlled explosions at AME Pte Ltd. and after (b) low-strength, (c) high-strength explosion with PETN.

observed for different explosive amounts. We found that the sample catchers were exposed to the same blast effects which occurred at a distance of around 50 cm from the source of explosion in the Bali bombing. For this comparison, we took into account only the amount and kind of explosive material assuming that both explosions with either 30 g or 5 kg of explosive material were high-strength explosions of spherically shaped charges.

The collection of post-blast debris of our test explosions was carefully done, keeping the debris that remained in the steel box separate from those ejected outside the box in order to minimize the risk of further contamination. Cotton sticks were also used for additional collection of traces from the surfaces of the containers.

#### 2.4. Sample preparation

During testing of post-blast residues embedded in different materials more than 200 samples were prepared and analyzed. For preparation, a small amount of less than 1 mg of high explosives material was taken and mixed with less than 100 mg of KBr powder. The mixtures were ground to fine powder until all visible crystallites disappeared and the mixture became “pasty” and stuck to the mortar. Next, the powder was put into a standard evacuable pellet press assembly, placed in a hydraulic press and compressed with a clamping force of 80 kN in order to produce a thin transparent pellet (diameter 13 mm, thickness less than 1 mm). The same procedure was applied to samples with macroscopic traces of explosive, especially after low-strength explosions.

When the explosive material was embedded in the surface of a sample catcher or no macroscopic traces of explosive materials were visible on these surfaces which was usually the case after a high-strength blast, a sterilized cotton stick wetted in acetone was used for swabbing, or the samples were thoroughly rinsed with acetone. In this case, explosive traces were recovered with the acetone solvent. Acetone was found to be a suitable solvent for the explosives because it is inert and does not react with them as proved by preliminary experiments that showed no additional lines in the FTIR spectrum of explosive material rinsed in acetone, in comparison with the FTIR spectra of a pure explosive. Acetone extracts were concentrated naturally by evaporating the solvent. KBr was added and the mixture was prepared in the same way as described earlier. However, it is worth saying that organic solvents like acetone are effective in dissolving explosive traces, but sometimes other compounds are recovered as well resulting in highly complex samples [28].

#### 2.5. FTIR analysis

FTIR analyses of samples were performed at the infrared spectro/microscopy beamline (ISMI) at SSLS. The end-station comprises a Bruker IFS 66 V/s FTIR spectrometer coupled to a Hyperion 2000 infrared microscope in one end and, in another end a high resolution Bruker IFS 125HR FTIR spectrometer. Both, an internal Globar source as well as infrared synchrotron radiation can be used. Owing to its high flux density, the infrared synchrotron radiation source provides a signal-to-noise ratio (SNR) of more than one order higher than the Globar source when using microscopic aperture, thus increasing the minimum detectability of samples. A more detailed description of ISMI may be found in [29].

The KBr pellet mixture was prepared from the collected residues found in the sample catchers as described earlier. The pellet sample was placed either into the sample compartment of the IFS 66 V/s FTIR spectrometer at base pressure (3 mbar) or placed in the sample stage of the infrared microscope for spectral acquisition. During all measurements, an MCT (Mercury Cadmium Telluride) detector cooled to liquid nitrogen temperature (77 K) was used. All transmission spectra were collected within the

spectral range of 4000 to 400  $\text{cm}^{-1}$  and about 600 scans were averaged at the resolution of 4  $\text{cm}^{-1}$ .

Measured spectra were analyzed using commercial Opus 6.0 software [30]. This analysis included a baseline correction, spectra normalization procedures, and peak-picking analysis for qualitative analysis. For a statistical treatment of the acquired spectra, an own database of FTIR spectra of pure explosive materials was constructed and the IDENT method [30] was used to identify and compare any collected spectrum with the available library.

### 3. Results

#### 3.1. FTIR of pure explosives

All spectra obtained by means of FTIR contain their own set of different peaks as a function of wavenumber [ $\text{cm}^{-1}$ ]. The relative peak height and the spectral position provide a unique characterization for any molecule that is infrared active. The infrared spectra of pure energetic materials measured at ISMI are in agreement with the spectra available in different databases, and their quality seems even better. Hence, in the present work, these “own” spectra were used as references in the further analysis of the post-blast residues. Fig. 3a displays the spectrum of pure PETN copied from the NIST database [31] and the spectrum of PETN measured at the ISMI beamline. A satisfactory agreement is observed.

Fig. 3b presents FTIR spectra of C-4 and TNT which were used as reference for further analysis. We note that the FTIR spectrum for C-4 (plastic explosive) is dominated mainly by the spectral signatures of its explosive component RDX, while additional lines in the regions at 1738  $\text{cm}^{-1}$  and around 2930  $\text{cm}^{-1}$  are contributed by vibrational modes of the plasticizer which was used in the production of C-4. Table 3 presents the vibrational frequencies of C-4, PETN and TNT observed in the FTIR spectra and their approximate assignments according to the literature [32–34]. These frequencies were used in the qualitative analysis of measured post-blast residue spectra.

#### 3.2. FTIR of post-blast residues—qualitative analysis of spectra

After each low-strength explosion, many macroscopic traces of explosives were found on different surfaces of catchers and their FTIR spectra were compared to spectra of pure explosives. All lines present in the appropriate reference spectrum also appear in the spectra after low-strength explosion. As an example, a comparison of the spectrum obtained from a plastic cover with the FTIR spectrum of pure PETN is shown in Fig. 4. For these spectra complete agreement was observed.

FTIR analysis also revealed the presence of explosives on different surfaces of materials even if they looked “clean” after low-strength explosion, thus no macroscopic traces were visible on their surfaces. As an example, a photo of an aluminum plate after a low-strength explosion with C-4 is shown as the inset in Fig. 5.

From Fig. 5, it can be seen that the FTIR spectrum of material collected from the aluminum plate matches the FTIR spectrum of pure C-4. All the lines which are present in the spectrum of pure C-4 are visible in the FTIR spectrum of the aluminum plate as well. Their line positions on the wavenumber axis ( $\text{cm}^{-1}$ ) and their relative intensities are also the same in comparison with the corresponding lines of C-4.

After high-strength explosions, no macroscopic traces of explosives on the surfaces of catchers could be found. Almost all catchers were covered by a dark layer of contamination caused by the blast; some of them were even seriously damaged. But even in these cases, further analysis resulted in detection and identification of traces of explosive material and allowed distinguishing the explosive materials from different contamination.

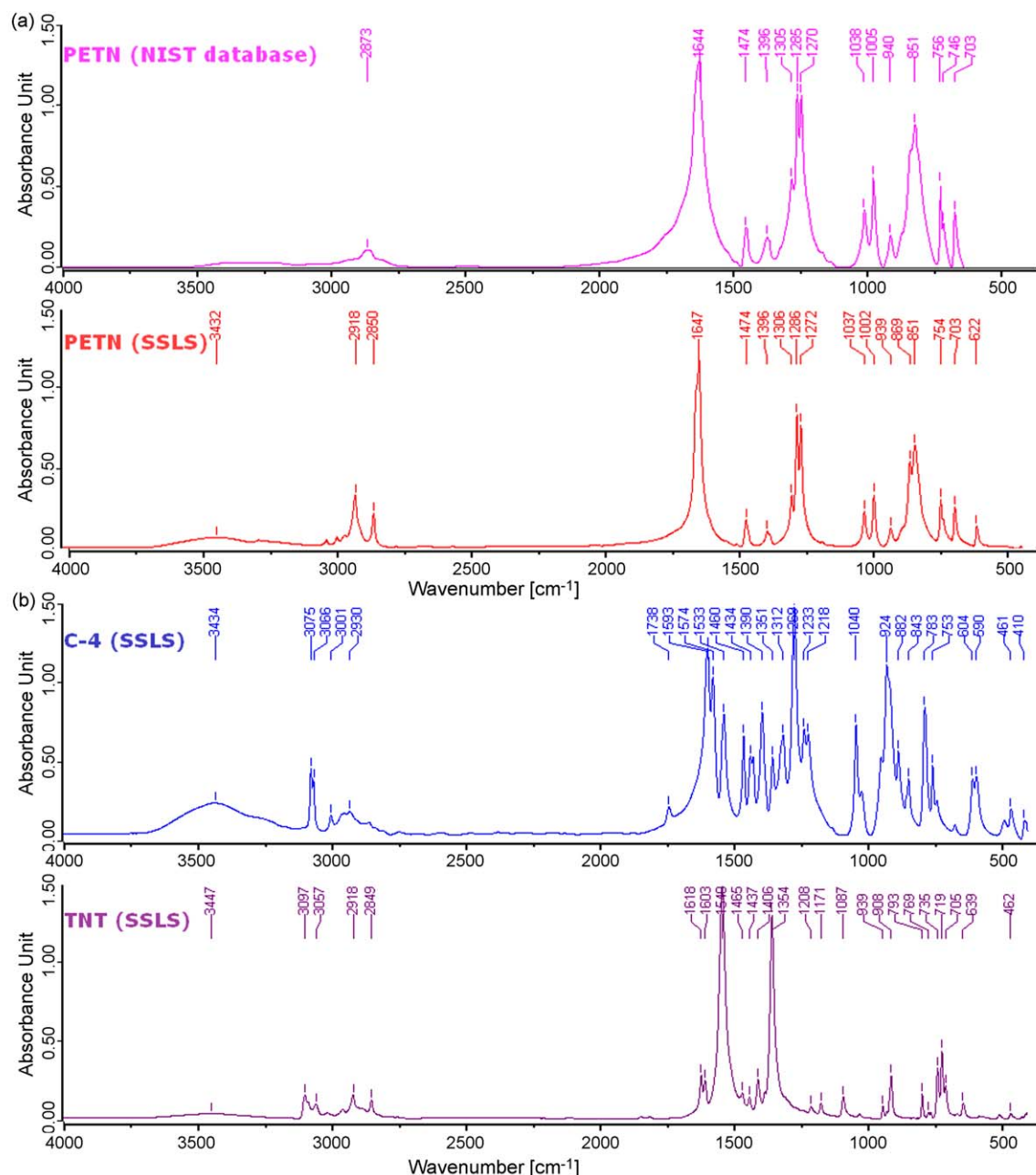


**Fig. 3.** FTIR spectra of (a) pure PETN from NIST database (upper panel) and measured at ISMI beamline at SSLS (lower panel), (b) C-4 (upper panel) and TNT (lower panel).

The inset in Fig. 6 presents a photo of a piece of plastic “foam” collected after a high-strength explosion with TNT. The FTIR spectrum obtained from trace materials taken from the surface of this “foam” contains almost all lines present in the FTIR spectrum of pure TNT as shown in Fig. 6. Apart from these characteristic lines, some additional lines, in particular in the region of 1400–800  $\text{cm}^{-1}$ , are observed. These additional lines may be attributed to other compound mixtures or reaction products as the “foam” was exposed to high temperature and pressure during the blast. But it is worth noticing that these additional lines do not mask the characteristic peaks of the explosive material.

### 3.3. Statistical analysis

The first step in the statistical analysis was the creation of a library of spectra of explosives used for the trials. The spectroscopic region 4000–400  $\text{cm}^{-1}$  was selected and each spectrum

from the samples of residues after the controlled explosions was compared with the spectra from the library by using IDENT method in OPUS software. The aim of an IDENT analysis was to determine the differences between a test spectrum and the reference spectra of the library. During comparison of an unknown spectrum to spectra from the library, the spectral distance  $D$  was calculated first. The spectral distance  $D$  is proportional to the area between two compared curves. In order to simplify the interpretation of the identity test results, vector normalization procedures were performed. Finally, the threshold was selected so that all original spectra used to create the reference spectrum (average spectrum) have a lower distance than this threshold to the reference spectrum. If the analysis of a sample spectrum produced a spectral distance which was larger than this threshold, the sample spectrum was defined as not being identical. Spectral distance was then translated into hit quality value which can be in the range from 0 denoting perfect match to 2 denoting a no match.

**Table 3**Experimental vibrational frequencies [ $\text{cm}^{-1}$ ] observed in FTIR spectra and their descriptions for high explosives: C-4, PETN, and TNT.

| Name of explosive   | Experimental vibrational frequencies [ $\text{cm}^{-1}$ ] | Description of the normal modes of vibration                 | Comments             |
|---------------------|-----------------------------------------------------------|--------------------------------------------------------------|----------------------|
| C-4 (composition 4) | 3075                                                      | CH stretch (s)                                               | Strong               |
|                     | 3066                                                      | CH stretch (a)                                               | Strong               |
|                     | 3001                                                      | Plasticizer                                                  | Weak                 |
|                     | 2930                                                      | Plasticizer                                                  | Weak                 |
|                     | 1738                                                      | Plasticizer                                                  | Weak                 |
|                     | 1593                                                      | NO stretch                                                   | Strong               |
|                     | 1574                                                      | NO stretch                                                   | Strong               |
|                     | 1533                                                      | NO stretch                                                   | Strong               |
|                     | 1460                                                      | H–C–N bend (a)                                               | Strong               |
|                     | 1434                                                      | H–C–N bend (a)                                               | Strong overlap       |
|                     | 1390                                                      | C–N stretch                                                  | Strong               |
|                     | 1351                                                      | C–N stretch                                                  | Strong               |
|                     | 1312                                                      | N–N stretch                                                  | Strong broad         |
|                     | 1269                                                      | C–N stretch                                                  | Very strong          |
|                     | 1233                                                      | C–N stretch                                                  | strong Overlap       |
|                     | 1218                                                      | C–N stretch                                                  | Strong overlap       |
|                     | 1040                                                      | C–N stretch                                                  | Strong               |
|                     | 924                                                       | O–N–O bend                                                   | Strong broad overlap |
|                     | 882                                                       | N–N–O bend                                                   | Medium               |
|                     | 843                                                       | N–N–O bend                                                   | Medium               |
|                     | 783                                                       | N–N–O bend                                                   | Strong               |
|                     | 753                                                       | Ring distortion                                              | Medium               |
|                     | 604                                                       | Chair type ring distortion                                   | Medium overlap       |
|                     | 590                                                       | Ring distortion at carbon atoms                              | Medium overlap       |
|                     | 461                                                       | Ring distortion                                              | Weak                 |
|                     | 410                                                       | Ring distortion                                              | Weak                 |
| PETN                | 2918                                                      | CH <sub>2</sub> stretch (a)                                  | Strong               |
|                     | 2850                                                      | CH <sub>2</sub> stretch (s)                                  | Strong               |
|                     | 1647                                                      | NO <sub>2</sub> stretch (a)                                  | Very strong          |
|                     | 1474                                                      | CH <sub>2</sub> scissors                                     | Strong               |
|                     | 1396                                                      | CH <sub>2</sub> wag + CCC def (CH <sub>2</sub> scissors def) | Weak                 |
|                     | 1306                                                      | CH <sub>2</sub> wag + C5 skeletal + NO <sub>2</sub> rock     | Medium overlap       |
|                     | 1286                                                      | NO <sub>2</sub> stretch + CH bend + C5 skeletal              | Very strong overlap  |
|                     | 1272                                                      | CH <sub>2</sub> bend + C5 skeletal + ONO <sub>2</sub> rock   | strong overlap       |
|                     | 1037                                                      | CO stretch + C5 skeletal + NO <sub>2</sub> rock              | Medium               |
|                     | 1002                                                      | CO stretch + CCC def                                         | Medium               |
|                     | 939                                                       | CH <sub>2</sub> torsion + CCC def                            | Weak                 |
|                     | 869                                                       | ON stretch                                                   | Weak overlap         |
|                     | 851                                                       | ON stretch                                                   | Strong overlap       |
|                     | 754                                                       | ONO <sub>2</sub> umbrella + CCC def                          | Strong               |
|                     | 703                                                       | ON stretch + CCC def + NO <sub>2</sub> rock                  | Strong               |
|                     | 622                                                       | CCC def + ONO <sub>2</sub> rock                              | Weak                 |
| TNT                 | 3097                                                      | C–H (ring) stretch (a)                                       | Weak                 |
|                     | 3057                                                      | C–H (methyl) stretch                                         | Weak                 |
|                     | 2918                                                      | C–H (methyl) stretch                                         | Weak                 |
|                     | 2846                                                      | C–H (methyl) stretch                                         | Weak                 |
|                     | 1618                                                      | C–C ring stretch                                             | Medium overlap       |
|                     | 1603                                                      | NO <sub>2</sub> stretch (a)                                  | Medium overlap       |
|                     | 1540                                                      | C–C ring stretch                                             | Very strong          |
|                     | 1465                                                      | CH <sub>3</sub> deformation                                  | Weak                 |
|                     | 1437                                                      | C–C ring stretch                                             | Weak                 |
|                     | 1405                                                      | Ring stretch                                                 | Medium               |
|                     | 1354                                                      | C–C ring stretch                                             | Very strong          |
|                     | 1207                                                      | C–C ring stretch                                             | Very weak            |
|                     | 1171                                                      | C–CH <sub>3</sub> stretch                                    | Very weak            |
|                     | 1087                                                      | C–H (ring) in plane bend                                     | Weak                 |
|                     | 1026                                                      | CH <sub>3</sub> deformation                                  | Very weak            |
|                     | 939                                                       | C–N stretch                                                  | Weak                 |
|                     | 908                                                       | C–N stretch                                                  | Medium               |
|                     | 793                                                       | C–C (ring) bending                                           | Medium               |
|                     | 769                                                       | C–C (ring) bending                                           | Weak                 |
|                     | 735                                                       | C–C (ring) bending                                           | Medium               |
|                     | 719                                                       | C–C (ring) bending                                           | Strong               |
|                     | 705                                                       | Ring torsion                                                 | Medium overlap       |
|                     | 639                                                       | C–C ring bending                                             | Small                |
|                     | 503                                                       | Ring torsion                                                 | Very small           |
|                     | 462                                                       | Ring torsion                                                 | Very small           |

The identity test routine generates a hit list which is stored in the IDENT report. Table 4 shows hit quality results for selected spectra of residues presented earlier.

In this way, a preliminary quantitative assessment of the presence of traces of explosive material in the spectra of debris was

obtained. This statistical analysis confirms the qualitative analysis of FTIR spectra performed earlier. The lowest value of hit quality for the FTIR spectra of plastic cover (0.0912) reveals the highest similarity of this spectrum to the FTIR spectrum for pure PETN. The lowest value of hit quality for the FTIR spectrum of plastic foam

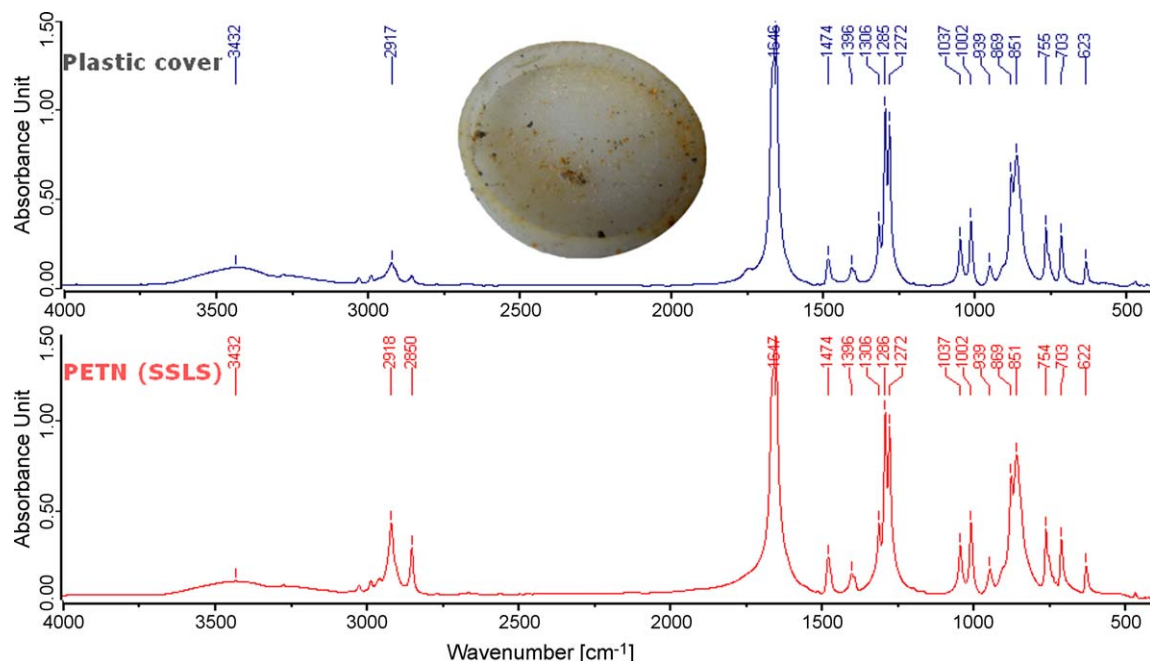


**Fig. 4.** FTIR spectra of residues taken from the surface of a plastic cover and pure PETN. The inset shows a plastic cover that was used as a sample catcher during a low-strength blast.

(0.4497) indicates the presence in this spectrum characteristic for pure TNT peaks. The fact that this value is not as small as for the other cases shown in the Table 4 may reflect the appearance of additional lines in the analyzed spectrum indicating the presence of compounds that might have existed before the blast or might be products of the explosion.

#### 4. Discussion

All FTIR spectra measured for samples collected after controlled explosions contain the spectral lines that are characteristic and unique for the appropriate explosives (C-4, PETN, TNT). This result

implies that many materials and objects of daily use can catch and store small amounts of explosives from a blast. They act effectively as “catchers” of explosives during a blast.

While being aware that we have identified explosives from post-blast residues in small explosions, we consider that this capability is necessary in order to eventually find them in large explosions. As a test of the methodology we took the opportunity to participate in a field test experiment performed by specialized police forces at a Police Training Camp, where a very large detonation of energetic material was done in open air, sample catchers were initially placed approximately 2 m away from the explosive site. Also in this case residues of the explosive material

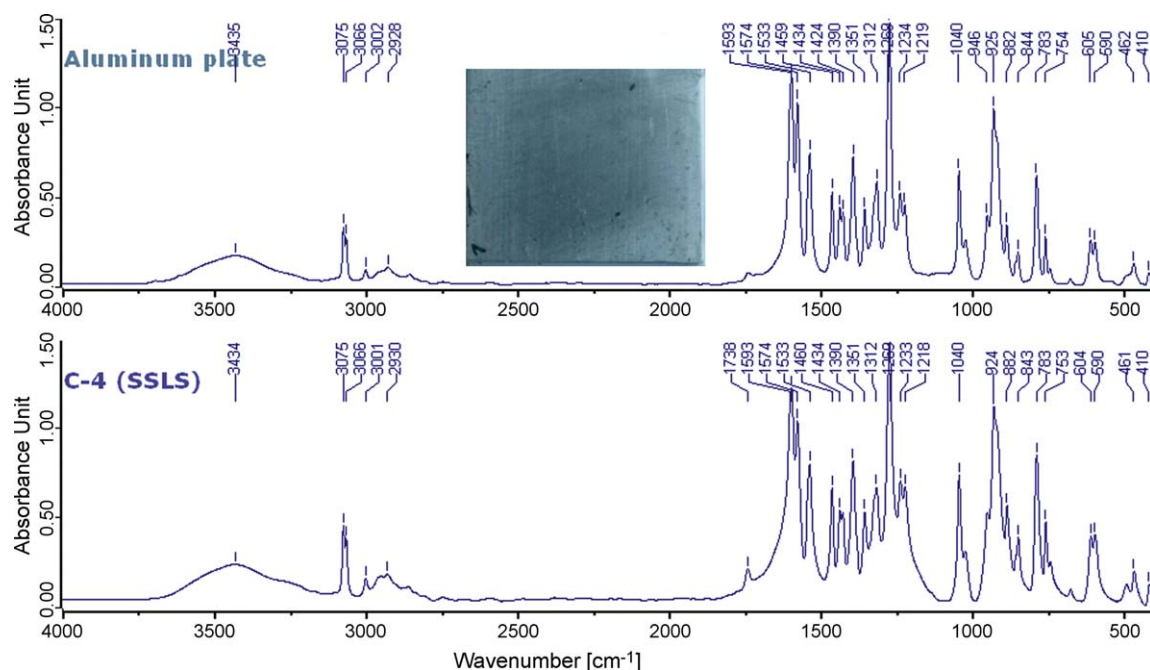


**Fig. 5.** FTIR spectra of material taken from the aluminum plate (presented as the inset) and pure C-4.

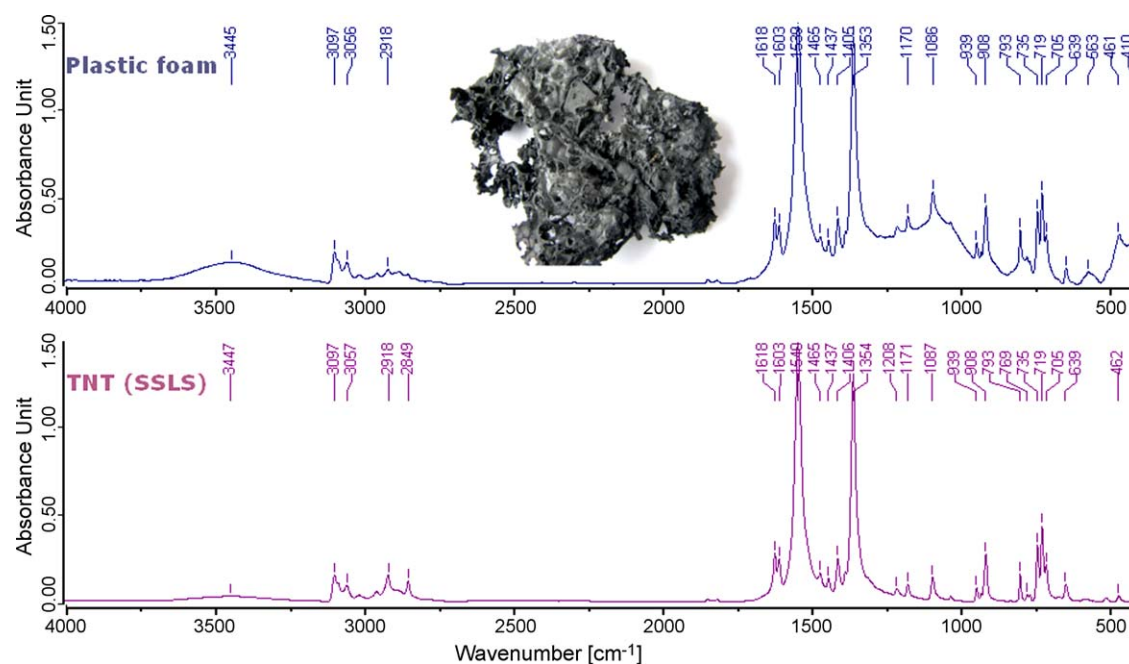


**Fig. 6.** FTIR spectra of material taken from plastic “foam” and pure TNT. Plastic “foam” as shown in the inset, was used as a sample catcher during a high-strength explosion with TNT.

**Table 4**

Comparisons of hit quality results for the spectra of residues collected after controlled explosions with the reference spectra of pure explosive materials.

| Name of the sample            | C-4    | PETN   | TNT    |
|-------------------------------|--------|--------|--------|
| Aluminum plate from C-4 blast | 0.0785 | 1.2894 | 1.2511 |
| Plastic cover from PETN blast | 1.2603 | 0.0912 | 1.4905 |
| Plastic foam from TNT blast   | 1.1792 | 1.5093 | 0.4497 |

were revealed with infrared technique endorsing the viability of the methodology presented.

It is worth saying that in the case of the present study of post-blast residues of explosives, most of the samples could be

satisfactorily measured with the Global source. However, when the samples are very small or dilute, then it becomes necessary to use synchrotron radiation (SR) as an infrared source. The superiority of synchrotron radiation infrared as compared to the Global in terms of the flux advantage in the far infrared and the brilliance advantage over the whole spectrum is well known [35].

As a demonstration, Fig. 7 presents an example of an experiment carried out on a very dilute RDX sample in transmission mode by means of the infrared microscope with slits set to  $7 \mu\text{m} \times 5 \mu\text{m}$ . It can be seen that only the use of SR guarantees the collection of FTIR spectra with well resolved peaks while spectra collected using the Global source have very low SNR which leads to the loss of all information about peaks belonging to analyzed

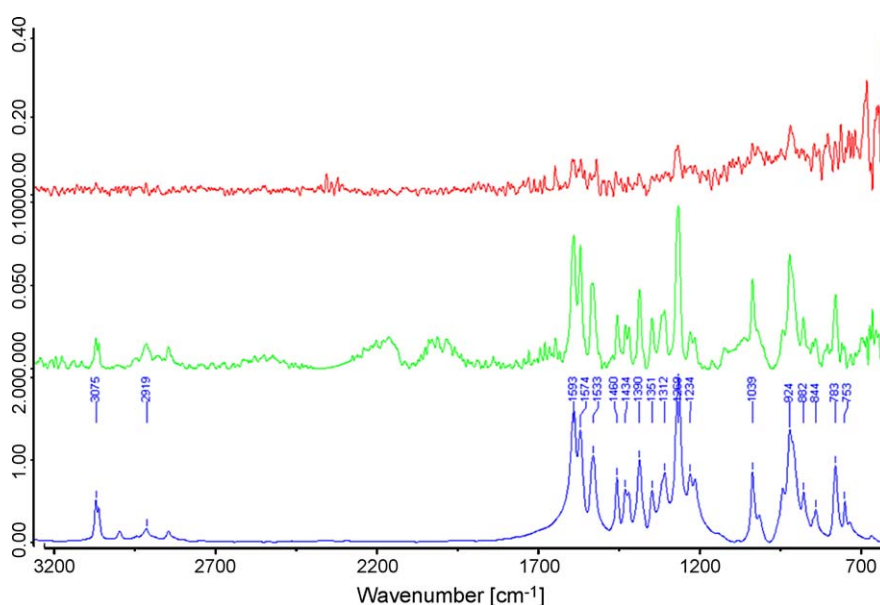


**Fig. 7.** FTIR spectra of very dilute sample of RDX in KBr pellet measured by means of Global (red line), and SR source (green line), in transmission mode with usage of microscope: slits were set to  $7 \mu\text{m} \times 5 \mu\text{m}$ . Dark blue line presents FTIR spectrum for RDX (reference spectrum). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

substance. According to the IDENT analysis, the hit quality calculated for the spectrum collected by means of SR is equal to 0.462 indicating high similarity of this spectrum to the FTIR spectrum of pure RDX. For the Globar spectrum this value is equal to 1.187, thus significantly worse.

## 5. Conclusion

Based on three high explosives that were available, we have proved that synchrotron-radiation-based Fourier transform infrared spectroscopy at SSLS can be used to identify and discriminate explosives on the basis of their characteristic fingerprint spectra, not only as pure crystalline materials, but also in real post-blast forms. Moreover, the universality of the method, high sensitivity, speed and repeatability of results make it an ideal tool for the examination of remains after an explosion in order to serve forensic purposes. In over 200 cases, the turn-around time to determine the explosive did not exceed half an hour. This method requires minimal amounts of samples and enables a very fast identification of the presence and the type of explosive material.

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