Chemical profiling of explosives
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Chapter 1

General introduction
1.1 Explosives in forensic casework

Explosives analysis is an important discipline present in many forensic-science laboratories. Although in most countries the case load in this field is relatively low compared to other disciplines, such as DNA or illicit drugs, the impact of cases involving explosives or explosions is often high. The criminal use of explosives is a global issue. Attacks are committed worldwide by terrorist organizations or individuals, mainly by the use of improvised explosives. Recent attacks include the bombing during the Boston Marathon in 2013, utilizing pressure-cooker bombs, and the attack on the government quarter in Oslo in 2011 with a fertilizer-based car bomb. Attacks on aircrafts were carried out using improvised explosive devices, hidden in either shoes (in 2002) or underwear (in 2009), but both attempts failed. These examples illustrate the need for improved detection and analysis of explosives.

Fig. 1.1. Typical forensic casework involving explosives: intact explosive material (a–c) with (a) plastic explosive Semtex, consisting of RDX and PETN; (b) a pipe bomb, often containing pyrotechnic material; (c) an IED based on PETN and the home-made explosive TATP as used by the shoe bomber; (d) a post-explosion crime scene (Oslo bombing); and (e) raw materials for the production of explosive devices.
Forensic cases that involve explosives may typically include post-explosion investigations, intact explosive devices, or materials possibly used to construct explosive materials or associated devices (Fig. 1.1). A wide variety of explosives is encountered in forensic casework, as a result of the alleged criminal use of military and commercial explosives that are obtained through illegal channels, or by the use of home-made explosives (Table 1.1). In general, military and commercial explosives are organic compounds with nitro groups, belonging to the nitramines, nitroesters or nitroaromatics (Fig. 1.2). One exemption is explosive-grade ammonium nitrate (AN), with applications in mining and civil construction [1,2]. The organic military and commercial explosives are generally characterized by high stability – required for safe handling and storage – and their high detonation velocities, depending on their specific application.

Fig. 1.2. Chemical structures of different types of organic explosives, categorized by their functional groups. Full names of the compounds are given in Table 1.1.
Table 1.1. Overview of the different types of explosives mentioned in this thesis, including their classification according to their use.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Full name(s)</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>Ammonium nitrate</td>
<td>Civil, home made</td>
</tr>
<tr>
<td>CL-20</td>
<td>Hexanitrohexaazaisowurtzitane</td>
<td>Military</td>
</tr>
<tr>
<td>DEGDN</td>
<td>Diethylene glycol dinitrate</td>
<td>Military, civil</td>
</tr>
<tr>
<td>EGDN</td>
<td>Ethylene glycol dinitrate</td>
<td>Military, civil</td>
</tr>
<tr>
<td>ETN</td>
<td>Erythritol tetranitrate</td>
<td>Home made</td>
</tr>
<tr>
<td>HMTD</td>
<td>Hexamethylene triperoxide diamine</td>
<td>Home made</td>
</tr>
<tr>
<td>HMX</td>
<td>Cyclotetramethylene tetranitramine;</td>
<td>Military</td>
</tr>
<tr>
<td></td>
<td>octogen</td>
<td></td>
</tr>
<tr>
<td>MEKP</td>
<td>Methyl ethyl ketone peroxide</td>
<td>Home made</td>
</tr>
<tr>
<td>NG</td>
<td>Nitroglycerine</td>
<td>Military, civil</td>
</tr>
<tr>
<td>PA</td>
<td>Picric acid</td>
<td>Military</td>
</tr>
<tr>
<td>PETN²</td>
<td>Pentaerythritol tetranitrate</td>
<td>Military</td>
</tr>
<tr>
<td>RDX</td>
<td>Cyclotrimethylene trinitramine;</td>
<td>Military</td>
</tr>
<tr>
<td></td>
<td>cyclonite; hexogen; research</td>
<td></td>
</tr>
<tr>
<td></td>
<td>department explosive</td>
<td></td>
</tr>
<tr>
<td>TATP</td>
<td>Triacetone triperoxide</td>
<td>Home made</td>
</tr>
<tr>
<td>TNT³</td>
<td>Trinitrotoluene</td>
<td>Military, civil</td>
</tr>
<tr>
<td>UN</td>
<td>Urea nitrate</td>
<td>Civil, Home made</td>
</tr>
</tbody>
</table>

In forensic casework, military explosives are often encountered as grenades or plastic explosives. Another class of explosives is the home-made explosives. Because access to military and civil explosives is restricted, improvised explosive devices (IEDs) are often constructed using more readily available materials. These include fertilizers, pyrotechnics, or peroxide explosives. Based on the chemical knowledge of the suspect, compounds such as PETN are occasionally encountered as a home-made explosive.

Fertilizer-based explosives are ammonium nitrate (AN), often mixed with a fuel, and urea nitrate (UN), obtained by nitration of the fertilizer urea. Because of their availability,
low sensitivity to shock and friction, and simple application, fertilizer-based explosives are typically used in large explosive devices. Examples of attacks involving fertilizer-based explosives are the Oklahoma City bombing in 1995 and the Oslo bombing in 2011. IEDs based on pyrotechnic material can contain fireworks ingredients or mixtures of raw materials, such as potassium or sodium chlorate, potassium perchlorate or potassium permanganate (oxidizers), sulfur and metal or metalloid powders (fuels) and various additives. An example of an attack involving a pyrotechnic mixture is the Bali bombings in 2002. Peroxide explosives can be synthesized using household chemicals, such as acetone, hydrogen peroxide and acid. The most frequently encountered peroxide explosives are hexamethylene triperoxide diamine (HMTD) and triacetone triperoxide (TATP). These explosives are characterized by their sensitivity to shock and friction and therefore production in large quantities is dangerous. Casework involving homemade explosives does not only comprise intact explosives or post-explosion residues, but frequently also raw materials.

1.1.1 Casework in the Netherlands
The Explosions and Explosives group at the Netherlands Forensic Institute (NFI) deals with about 200 cases per year. Approximately 60% of these involve intact explosive devices, such as IEDs, grenades and illegal fireworks (Fig. 1.3). Other types of casework include the examination of parts of intact explosive devices (~10%), such as high-explosive (HE) substances and blasting caps, post-explosion casework (~15%) and identification of possible precursors for explosives (~10%). The other 5% of the cases include, for example, assistance on crime scenes and sampling of suspects for the presence of traces of explosive material.

In the period of 2009−2013, a total of 58 cases were submitted to the NFI involving intact high-explosive substances, compared to 31 post-explosion cases. Four cases included both intact explosives and post-explosion material. In total, 28 intact hand grenades were encountered, as well as more than 70 blasting caps and close to 50 plastic explosives. An overview of the different types of high explosives encountered in pre- and post-blast casework is given in Fig. 1.4. This figure illustrates that the most frequently encountered
high explosive in the Netherlands is PETN, followed by TNT, RDX and HMX. Note that cases involving pyrotechnics are not included in the figure.

Fig. 1.3. Average caseload in the Explosions and Explosives group at the NFI in the period 2010-2013. The types of explosives are specified for intact explosives and post-explosion casework. ‘HE’ stands for high explosives and ‘other’ largely concerns pyrotechnics.\(^4\)

Fig. 1.4. Frequency of encountering specific types of high-explosives in the period 2009–2013 in cases submitted to the NFI for intact explosives and post-explosion samples.

\(^4\) IEDs based on pyrotechnic material, either home-made or originating from fireworks ingredients.
1.2 Forensic explosives analysis

The choice of analytical techniques to study an explosive material depends on its nature (bulk material or residues) and on its type (organic or inorganic). Beveridge [3] and Yinon [4] provide overviews of the analytical techniques used. Various techniques can be used for the analysis of bulk explosive material. Infrared and Raman spectroscopy can be employed for the identification of both inorganic and organic materials [5] – either in the laboratory or in the form of portable instruments for on-site detection of explosives [6]. X-ray diffraction (XRD) can also be used for the analysis of inorganic and organic materials, provided that the material is crystalline. Information on the elemental composition of inorganic intact explosives can be obtained by X-ray fluorescence (XRF).

In case of material that is suspected to be of pyrotechnic nature, small-scale burn tests can be performed to test whether the ingredients are mixed in the appropriate ratio to yield an effective pyrotechnic composition. In addition, the burning behavior of the material gives an indication of its chemical composition.

Analysis of residues from organic explosives is usually performed using high-performance liquid chromatography (HPLC) or gas chromatography (GC). Various detection methods have been employed, such as photo-diode array (PDA) detection for HPLC and the thermal-energy analyzer (TEA) [7], a detector exhibiting a high selectivity and high sensitivity for nitro and nitroso groups, and the electron-capture detector (ECD) for GC analysis. However, current research mostly relies on mass spectrometric (MS) detection, as it provides high sensitivity, high selectivity and structural information. GC instrumentation is more widely available than LC in many forensic laboratories due to lower costs, faster analyses, robustness, and easier coupling with MS, but it operates at higher temperatures, rendering the analysis of thermolabile explosives (e.g. RDX, HMX and PETN) difficult [4,8-10]. Therefore, LC–MS is generally the method of choice for identification of organic explosives [11,12]. Residues of inorganic explosives are best analyzed using ion chromatography (IC) [13,14], offering high sensitivity and repeatability, or capillary electrophoresis (CE), providing short analysis times and application in portable devices [15]. Because these techniques
are based on complementary separation mechanisms, they are often used in parallel for confirmation of the identification of inorganic explosives [13,14]. It should be noted that interpretation of analytical results involving inorganic residues is complicated by the natural occurrence of these materials. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDS) has been employed for the elemental analysis of pyrotechnic residues [16,17]. Although the aforementioned techniques are routinely used in forensic laboratories, recent research explored the use of techniques such as laser-induced breakdown spectroscopy (LIBS) [18], direct analysis in real time MS (DART–MS) [19] and secondary-ion MS (SIMS) [20] for the detection and identification of explosives.

All of the aforementioned approaches focus on identification of the explosive material. A major trend emerging in forensic science in general is individualization, which is necessary when investigating relationships between material recovered from a crime scene (e.g. an explosive device) and material associated with a suspect (e.g. explosive material or raw materials). Basic identification does not suffice to study such relationships. Chemical profiling can be an important tool for individualization of the material.

1.3 Chemical profiling in forensic science

According to Inman and Rudin [21], individualization is “the ultimate goal of a forensic examination”. To achieve individualization, properties need to be determined that are characteristic for a common source (e.g. a chemical profile). In casework, the evidential value of matching characteristics can be assessed according to Bayes’ theorem using likelihood ratios (LR). Bayes’ theorem is described in detail by Aitken and Taironi [22], Berger [23] and Inman and Rudin [21]. This theorem indicates that true individualization does not exist in forensic science as there is never absolute certainty on the existence of a relationship between materials. However, the term illustrates the quest for chemical profiling methods that establish strong support for such a relationship. The probability of the evidence (e.g. a matching profile) needs to be viewed in light of two hypotheses: (1) the questioned sample (i.e. crime-scene sample) originates from the same source as
the reference sample (i.e. suspect’s sample) and (2) the questioned sample originates from another source. To determine the likelihood of a matching profile, background information is needed on the occurrence of typical profiles for both hypotheses. This means that samples originating from the same source should be studied to determine the within-source variation, and samples from different sources to establish the between-source variation. To accurately model the within- and between-source variations, sufficiently large sample sets are required. Considering the relatively low numbers of cases and amounts of explosives in circulation, chemical profiling of explosives is challenging. Chemical profiling is more advanced in other forensic disciplines, such as drug analysis, where the caseload and sample throughput are higher. In addition, most types of drugs are organic substances that are volatile, or can be made volatile through derivatization, and can therefore be analyzed using a single analytical technique (i.e. gas chromatography), in contrast to explosives as described in section 1.2. Individualization using GC-based impurity-profiling methods has been achieved for different types of drugs, mainly for MDMA (3,4-methylenedioxy-N-methylamphetamine, known as ecstasy or XTC) [24] and other amphetamines [25], but also, for example, for heroin [26] and cocaine [27]. In addition, impurity profiles proved to be useful for deducing the synthetic route and type of precursors used, implying that impurity profiling cannot only be used as evidence in court, but also for intelligence purposes [28]. This illustrates the importance of using knowledge on production processes and distribution of the material to understand and interpret chemical profiles.

As described above, individualization deals with establishing the source or origin of questioned samples. The hypotheses are therefore constructed at source level. However, according to the hierarchy of propositions [21], hypotheses can be proposed at two other levels, i.e. activity level and offense level. Besides individualization, moving towards evaluation of the evidence on the activity level is another major trend in contemporary forensic science. An interesting example is shown in the area of DNA analysis. Matching DNA profiles are routinely used to define the source of a biological trace. The recent development of RNA typing enables determination of the cell type, thus providing
valuable information regarding the activity that led to the suspect’s DNA on the crime scene or evidence items [29].

1.4 Chemical profiling of explosives

Several studies have been aimed at chemical profiling of explosives. The majority of these studies focused on the use of isotope-ratio mass spectrometry (IRMS). Small variations occur in the isotopic composition of materials based on their origin and history. Based on the isotopic composition it was possible to discriminate between different batches of both organic and inorganic explosives, such as Semtex [30], triacetone triperoxide (TATP) [31], pentaerythritol tetranitrate (PETN) [31,32], black powder, flash powder, nitromethane, plastic explosive no. 4 (PE4) [33], trinitrotoluene (TNT) [32-34] and ammonium nitrate [32,35]. In addition, it was shown that the isotopic signatures of the explosives cyclotrimethylenetrinitramine (RDX) [36] and urea nitrate [37] depend on the isotopic composition of the precursors. This information can be used to establish a chemical link between an explosive from a crime scene and precursors seized from a possible suspect.

Besides the isotopic signatures that may vary based on the precursors used and the synthesis mechanisms, other characteristics of explosive samples are impurities that can be introduced into the sample during synthesis, are formed due to degradation over time, or result from contamination in the presence of other materials. TNT samples from different origins showed varying by-product profiles based on the presence of dinitrobenzene, dinitrotoluene, trinitrobenzene and trinitrotoluene isomers detected using LC–MS [38]. For the home-made explosives HMTD and TATP it was observed that impurities present in improvised sources of the precursor hydrogen peroxide (e.g. hair-bleaching products) could be detected using GC–MS after the synthesis of the home-made explosives HMTD and TATP [39]. These impurities could even be detected after initiation of the HMTD and TATP, giving an indication of the type of precursors used for production of the explosive device. Benson et al. [35] studied the possibility to link post-blast ammonium nitrate (AN) to the intact AN used for the explosion using IRMS. Post-
blast AN was found to be more enriched in $^{15}$N compared to pre-blast AN, but there was no clear relationship between the post and pre-blast samples. Relationships between the isotopic composition of post-explosion samples and the corresponding intact explosive could also not be established for different types of organic explosives [40]. McGuire et al. [40] suggested that post-explosion samples originating from aromatic explosives could be distinguished from non-aromatic explosives based on their carbon isotope ratios, but this can also easily be accomplished using, for example, LC–MS. Post-explosion profiling is difficult because of possible interference by environmental contaminants. In addition, as far as isotope analysis of post-explosion material is concerned, isotope exchange with the atmosphere may occur. Isotope fractionation during an explosion is difficult to predict and is likely to be irreproducible, because of the uncontrolled nature of an explosion.

As discussed above, most of the studies concerning the chemical profiling of explosives focus on comparison of different batches of the explosive. Knowledge on the chemical processes used in the manufacturing of explosives is important to understand and interpret the chemical profiles. Most of the studies used sample sets consisting of only a few samples. This limits these studies in determining the evidential value of eventual inferences.

### 1.5 Scope of this thesis

This thesis focuses on novel applications of chemical profiling of explosives for forensic purposes. This includes development of analytical methods for profiling as well as evaluation of the results from a forensic point of view. Various approaches are considered with respect to utilizing sufficiently large sample sets to establish or indicate evidential values of matching profiles, evidence evaluation at activity level and studying relationships between home-made explosives and their associated precursors.

In Chapter 2 we describe the use of vacuum-outlet GC–MS for impurity profiling of TNT to discriminate between different sources of the explosives. This approach is
similar to the approach used for illicit drugs as described in section 1.3. Depending on the synthesis and clean-up procedures and possible degradation, impurities can be introduced in TNT, resulting in characteristic profiles for samples with different origins and histories. Vacuum-outlet GC–MS provides short analysis times and is promising for the analysis of thermolabile explosives because of low elution temperatures. Studying the variation in impurity profiles between samples from the same origin and between samples from different origins allows assessing the evidential value of matching profiles in terms of likelihood ratios.

Chapter 3 focuses on profiling of PETN and its common degradation products pentaerythritol trinitrate (PETriN), pentaerythritol dinitrate (PEDI N) and pentaerythritol mononitrate (PEMN). In NFI casework, LC–MS had been used to identify PETN and its degradation products on the clothing of a suspect allegedly involved in a series of safe crackings. As the suspect denied his involvement it was questioned whether the identified degradation products were a result of a PETN explosion. In this perspective, differences between post-explosion PETN, intact PETN and naturally-degraded PETN are studied using LC–MS. It is demonstrated that this information can be used to investigate possible crime-scene presence of a suspect and therefore to evaluate the evidence on activity level. However, the unavailability of commercial standards of the degradation products of PETN rules out accurate quantitative analysis. This latter issue is addressed in Chapter 4, where we describe accurate quantitation based on the use of custom-made standards. This renders the discrimination between post-explosion PETN and naturally degraded PETN more robust.

The relationship between the isotopic composition of the explosive HMTD and its precursors are studied using isotope-ratio MS in Chapter 5. The general availability of precursors makes HMTD popular as home-made explosive. Several batches of HMTD are synthesized with precursors from different origins. In addition, the influence of varying synthesis conditions (relevant to more or less realistic crime-scene circumstances) on the isotopic composition of HMTD is investigated.
In Chapter 6 isotope and elemental analysis were combined for the chemical profiling of ammonium nitrate (AN). AN is popular for application in explosive devices, because of its explosive properties and it is widely available as fertilizer. The geographical origin of AN may be reflected in its isotopic composition, whereas raw materials used in the manufacturing of AN may result in characteristic elemental profiles. Therefore, IRMS is employed to determine the isotopic composition of AN and the trace-elemental composition of AN is studied using inductively-coupled plasma with MS detection (ICP–MS). In addition, the potential of laser-ablation ICP–MS for elemental profiling of single AN granules is investigated.

The chapters of this thesis have been prepared for publication in international scientific journals and can be read independently. Therefore, some overlap may occur.
References


