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Chemical Profiling of Explosives
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Summary

PhD thesis Hanneke Brust
Chemical profiling of explosives

The primary goal of this thesis is to develop analytical methods for the chemical profiling of explosives. Current methodologies for the forensic analysis of explosives focus on identification of the explosive material. However, chemical profiling of explosives becomes increasingly important, as this allows studying relationships between explosive material found on a crime scene and material associated with a suspect. A range of approaches to chemical profiling is explored in this thesis for various purposes and various types of explosives. Chemical profiling is used to study relationships between two explosives samples (*i.e.* a crime-scene sample and a sample from a suspect) and between a home-made explosive and its precursors. In addition to these 'source-level' comparisons, we also demonstrate the use of chemical profiling for 'activity-level' investigations (studying crime-scene presence).

The wide variety of techniques currently used in forensic explosives analysis is discussed in *chapter 1*. In addition, the concept of individualization is introduced and an overview is presented on chemical profiling in forensic science, as well as specific examples for explosives. Previous research on chemical profiling of explosives has mainly focused on isotope-ratio mass spectrometry (IRMS). However, the use of small sample sets limits the capability of this technique for assessing the evidential value of matching characteristics.

A vacuum-outlet gas chromatography–mass spectrometry (GC–MS) method for impurity profiling of trinitrotoluene (TNT) is presented in *chapter 2*. TNT is a military explosive frequently encountered in forensic casework. Vacuum-outlet GC–MS allows short analysis times and impurity profiles of TNT can be obtained within four minutes. Several impurities have been detected, including 1,3-dinitrobenzene, 2,3,4-trinitrotoluene, two different amino dinitrotoluene isomers and several dinitrotoluene isomers. The levels of these compounds showed significant variations in the different samples. This information can be used to determine whether TNT samples originate from a common source. A discussion on the evidential value of a matching impurity profile in terms of likelihood ratios is provided.

In *chapter 3* it is investigated whether residues from the explosive pentaerythritol tetranitrate (PETN) on clothing of a suspect originate from an explosion or from intact or naturally degraded PETN. For this purpose, explosion experiments have been conducted, as well as simulated degradation experiments. Using liquid chromatography–mass spectrometry (LC–MS), the degradation products pentaerythritol trinitrate (PETriN), pentaerythritol dinitrate (PEDiN) and pentaerythritol mononitrate (PEMN) are identified. It is observed that the levels of these degradation products relative to PETN are much higher for post-explosion samples than for intact PETN or for naturally-degraded PETN. A robust profiling method requires accurate

quantitation of the degradation products. Standards of PETriN, PEDiN and PEMN were not commercially available and variations in LC–MS response factors of these compounds relative to PETN have been observed over time. Therefore, standards of PETriN, PEDiN and PEMN have been synthesized. As described in *chapter 4*, these custom-made standards allowed us to rigorously study the analytical behavior of these compounds and to accurately quantify their levels in degraded PETN samples. The results demonstrate that it is possible to establish whether a suspect with residues on his clothing has been present at a PETN explosion scene (activity level).

The use of isotope-ratio mass spectrometry (IRMS) to study relationships between the home-made explosive hexamethylene triperoxide diamine (HMTD) and its precursors is described in *chapter 5*. HMTD has been synthesized using precursors with different origins and all precursors and HMTD have been analyzed using IRMS. Relationships between carbon and nitrogen isotope ratios of the precursor hexamine and the HMTD product are observed, although the shift in isotopic composition from precursor to product changes when synthesis conditions are varied. However, in all cases HMTD is found to be enriched in ^{15}N and depleted in ^{13}C compared to its precursor hexamine. Therefore, relationships between HMTD and precursor material provide useful information for forensic investigations, especially in the exclusion process.

In *chapter 6* we explore the use of IRMS and inductively-coupled plasma with mass-spectrometric detection (ICP–MS) for profiling of ammonium nitrate. Ammonium nitrate is widely available as fertilizer and often applied in explosive devices. AN samples from different product classes and production locations have been obtained from fertilizer manufacturers. Elemental profiles measured using ICP–MS are shown to be characteristic for specific samples of AN. The isotopic composition of ammonium nitrate is found to mainly depend on the production location. Combining the complementary information on the origin of an AN sample obtained from isotopic and elemental profiling is shown to be a powerful tool for discriminating between different types of AN and AN from different manufacturers. Linear discriminant analysis was used to calculate the evidential value of matching profiles in terms of likelihood ratios.