Chemical profiling of explosives
Brust, G.M.H.

Citation for published version (APA):
Brust, G. M. H. (2014). Chemical profiling of explosives

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 4

Accurate quantitation of pentaerythritol tetranitrate and its degradation products using LC–APCI–MS

This chapter has been published as:
H. Brust, A. van Asten, M. Koeberg, J. Dalmolen, A. van der Heijden, P. Schoenmakers

Abstract

After an explosion of pentaerythritol tetranitrate (PETN), its degradation products pentaerythritol trinitrate (PETriN), dinitrate (PEDiN) and mononitrate (PEMN) were detected using liquid chromatography–atmospheric-pressure chemical-ionization–mass spectrometry (LC–APCI–MS). Discrimination between post-explosion and naturally-degraded PETN could be achieved based on the relative amounts of the degradation products. This information can be used as evidence when investigating a possible relationship between a suspect and a post-explosion crime scene. This chapter focuses on accurate quantitation of PETN and its degradation products, using PETriN, PEDiN and PEMN standards specifically synthesized for this purpose. With the use of these standards, the ionization behavior of these compounds was studied, and a quantitative method was developed. Quantitation of PETN and trace levels of its degradation products was shown to be possible with accuracy between 85.7% and 103.7% and a precision ranging from 1.3% to 11.5%. The custom-made standards resulted in a more robust and reliable method to discriminate between post-explosion and naturally-degraded PETN.
4.1 Introduction

Forensic explosives analysis usually comprises the identification of the explosive compound that has been used. However, much more information is usually contained in samples collected during the investigation. For example, the presence of impurities or degradation products may yield valuable information on the origin or history of the sample. Chemical profiling can be used to study this origin-related information. The choice of analytical methodology depends on the type of explosive compound under investigation. While gas chromatography mass spectrometry (GC–MS) is suitable for the analysis of nitroaromatic explosives, nitroester and nitramine explosives are thermolabile and have low vapor pressures and, therefore, their analysis with GC–MS is difficult. For analysis of pentaerythritol tetranitrate (PETN), which belongs to the class of nitrate-ester explosives, liquid chromatography–mass spectrometry (LC–MS) is a more suitable technique. Variations in response have been observed when analyzing PETN and related compounds with mass spectrometry (MS), as described in chapter 3. In this respect the ionization in the LC–MS interface is an important factor.

The high electron affinity of the nitro groups makes these compounds suitable for analysis in negative-ion mode [1-4]. Although electrospray ionization (ESI) has been shown to be a slightly better ionization technique for PETN and other nitrate esters [1,2], atmospheric-pressure chemical ionization (APCI) enables ionization of all explosive compounds [2-4] and hence APCI was used in this research. Formation of [M–H]- ions is difficult for PETN and other nitrate-ester explosives. In general, mass spectra of these compounds show signals corresponding to a variety of adducts, resulting from impurities in the mobile phase [1,5]. Sensitivity of compounds lacking acidic sites can be improved by introducing an additive that promotes specific adduct formation [6]. For ESI the most sensitive detection of nitrate-ester explosives was achieved when nitrate adducts were formed [1,7], while for APCI chloride-adduct formation was more successful [1]. Chloride-adduct formation of PETN analyzed using LC–APCI–MS was achieved in several studies using chloroform or ammonium chloride [1,8], methylene chloride [9], dichloromethane [1,10] or carbon tetrachloride [1,5] as additives. Zhao and Yinon [1]
concluded that ammonium chloride and chloroform provided the best sensitivity for the nitrate esters PETN, ethylene glycol dinitrate (EGDN) and nitroglycerin (NG).

In the previous chapter we have described the discrimination between post-explosion PETN and naturally-degraded PETN based on LC–MS peak-area ratios of the degradation products pentaerythritol trinitrate (PETriN), pentaerythritol dinitrate (PEDiN) and pentaerythritol mononitrate (PEMN) (see Fig. 4.1 for chemical structures) relative to PETN. This information can be used when investigating a possible link between a suspect with residues of PETN on his or her personal items or clothing and a post-explosion crime scene. In the absence of commercially available standards of the PETN degradation products, degradation and post-explosion profiles were based on peak-area ratios. However, variations in peak-area ratios were observed over time, probably due to compound-specific variations in MS response factors. To investigate these variations in more detail, custom-made standards for the PETN degradation products were synthesized. This chapter describes the use of these standards for accurate quantitation of PETN and its degradation products in residue extracts. Ionization of these compounds and the associated sensitivity and repeatability could be studied in detail. These new insights allowed to further validate the methodology for establishing crime-scene presence.

4.2 Experimental

4.2.1 Chemicals and materials

The custom-made standards of PETriN, PEDiN and PEMN were prepared by Syncom (Groningen, The Netherlands) as described in section 4.2.2. Stock solutions of 1 mg/mL were made in HPLC-grade methanol (Rathburn, Walkerburn, UK). High-purity PETN (containing a low level of PETriN as a minor impurity) was provided by TNO, Department of Energetic Materials (Rijswijk, The Netherlands). We used a commercially-available analytical standard of PETN (AccuStandard, New Haven, CT, USA) and compared its purity with that of the PETN reference material obtained from TNO. All standard and sample solutions were prepared as 1:1 mixtures of methanol.
and ultra-pure water, obtained from a Milli-Q (Millipore, Bedford, MA, USA) or a PureLab Ultra (Elga, High Wycombe, UK) system, to ensure compatibility with the mobile phase. Calibration curves were constructed using mixtures of PETN, PETriN, PEDiN and PEMN at different concentrations (0.05–5 ppm for PETN, 0.01–1 ppm for PETriN, 4–400 ppb for PEDiN and 2–200 ppb for PEMN). The concentrations used for the calibration solutions are consistent with the levels of the compounds detected in post-explosion samples and natural-degradation samples during previous work.

4.2.2 Custom-made standards

PETriN, PEDiN and PEMN were synthesized by Syncom (Groningen, The Netherlands). Ueno et al. [11] described the reaction of pentaerythritol with \( t \)-butylchlorodiphenylsilane to form a mixture of tri-, di- and mono-protected pentaerythritol, which could be separated using preparative column chromatography. Nitration of the remaining hydroxyl groups and subsequent removal of the silyl protective groups according to Farcy et al. [12] yielded PETriN, PEDiN and PEMN. The reaction mechanism of the synthesis of PETriN, PEDiN and PEMN is shown in Fig. 4.1. \(^1\)H-NMR spectra were provided demonstrating the purity of the three compounds. These spectra were recorded on a Varian VXR-300 spectrometer (300 MHz). Chemical shifts are denoted in parts per million (\( \delta \)) and are referenced to the residual solvent. Coupling constants \( J \), are denoted in Hz and splitting patterns are designated as follows: s (singlet); d (doublet); dd (double doublet); t (triplet); dt (double triplet); q (quartet); m (multiplet) and brs (broad singlet).

**PEMN** (brown oil); \(^1\)H-NMR (300 MHz, [D6]-DMSO): \( \delta = 3.36 \) (d, 6H, \( J = 5.42 \) Hz), 4.44 (s, 2H), 4.55 (t, 3H, \( J = 5.42 \) Hz) ppm.

**PEDiN** (yellow oil); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 1.93 \) (brs, 2H), 3.80 (s, 4H), 4.58 (s, 4H) ppm.

**PETriN** (yellow oil); \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 1.76 \) (t, 1H, \( J = 4.7 \) Hz), 3.78 (d, 2H, \( J = 4.7 \) Hz), 4.57 (s, 6H) ppm.
4.2.3 Simulated samples

To examine the performance of different calibration methods, samples were prepared using the custom-made standards, containing levels of PETN, PETriN, PEDiN and PEMN similar to those previously detected in post-explosion and natural-degradation samples. The actual levels were estimated using the PETN calibration data obtained during analysis of the simulated samples and the relative response factors of PETriN, PEDiN and PEMN obtained during this research. The simulated samples were prepared at high (4, 0.3, 0.12 and 0.06 ppm), medium (1.6, 0.15, 0.06 and 0.03 ppm) and low (1, 0.08, 0.032 and 0.016 ppm) concentrations of PETN, PETriN, PEDiN and PEMN, respectively. Accuracy and precision of the calibration method were determined by analyzing the simulated samples of known concentrations on five different days.

Fig. 4.1. Synthesis procedure of custom-made standards of pentaerythritol trinitrate (PETriN), pentaerythritol dinitrate (PEDiN) and pentaerythritol mononitrate (PEMN). The inset shows the chemical structure of PETN.
4.2.4 Matrix effects

The influence of three different matrices relevant to this research (sterile gauzes, acrylic textile and soil) on the analysis of degraded PETN samples using LC–MS was examined. Sampling after an explosion is usually done by swabbing with the sterile gauzes (Klinion NW Compres 50 × 50 mm, Medeco, Oud-Beijerland, The Netherlands) wetted with methanol. The acrylic textile was included to resemble clothing of a suspect from which samples can be taken. Although soil is an unlikely matrix in cases in which the presence of a suspect on a crime-scene is questioned, its influence on the analysis was tested because it is considered to be a dirty matrix. In addition, the influence of soil matrix is of interest, because soil samples can be collected on a post-explosion crime scene or soil may be found on the shoes of a suspect. The soil was obtained from TNO. Blank extracts of the three matrices were prepared by extraction with 10 mL of methanol and ultrasonication for 30 min. The extracts were filtered through a 0.45 µm regenerated cellulose (RC) filter (Whatman, Dassel, Germany). Blank extracts of the matrix material were spiked with mixtures of PETN, PETiN, PEDiN and PEMN at the high and low concentrations as described in section 4.2.3 and compared to a methanol-water solution containing the same levels of the four compounds. The purpose was to test the influence of the matrix on the analytical method. Matrix effects during extraction on the recovery of these compounds are therefore not included in this work.

4.2.5 LC–MS analysis

All samples were analyzed on a Thermo Fisher Scientific (Waltham, MA, USA) Surveyor HPLC Plus system with a PDA detector, connected to a Thermo Scientific LTQ Orbitrap XL mass analyzer. Separation was performed on a LiChrospher RP18 analytical column (Merck, Darmstadt, Germany; 2 × 250 mm, \(d_p\) 5 µm) equipped with a Phenomenex (Torrence, CA, USA) Securityguard C18 guard column (4 × 2 mm, \(d_p\) 5 µm). The column temperature was maintained at 35°C. The mobile phase consisted of water and methanol, using a gradient at a flow rate of 200 µL/min. The following gradient was used: 0–2 min, 45% MeOH; 2–15 min, 45%–90% MeOH linear; 15–20 min, 90% MeOH; 20–25 min, 45% MeOH. Four percent chloroform in methanol were added post column (2 µL/min) to enhance negative-ion yield by the formation of stable
chloride adducts. The injection volume was 10 µL (partial-loop injection mode). The MS was operated in negative mode using an APCI ion source. MS instrument settings are summarized in Table 3.1.

![Mass spectra](image)

Fig. 4.2. Mass spectra of PETN (a), PETriN (b), PEDiN (c) and PEMN (d). Conditions as described in section 4.2.5.

### 4.3 Results and discussion

#### 4.3.1 Characterization of PETriN, PEDiN and PEMN custom-made standards.

The purity of each custom-made standard was confirmed using LC–MS. From the synthesis mechanism, possible impurities in the standards could be any of the other nitrate esters, but neither these, nor other impurities were detected. The purity and LC–MS response of the PETriN custom-made standard were checked against the commercial PETriN standard from AccuStandard, which recently became available.
The commercial PETriN standard showed a low amount of PEDiN (< 1%) as impurity. This was not detected in the custom-made standard. MS-response for the custom-made PETriN standard was 99.8% compared to the commercial standard. The observed high purity of the custom-made standards is in agreement with the $^1$H-NMR spectra provided by Syncom.

![Fig. 4.3. Extracted-ion chromatogram (m/z 350.9833; 305.9982; 261.0131 and 216.0281) of a mixture of PETN, PETriN, PEDiN and PEMN, containing 1.25 ppm of each analyte. Conditions as described in section 4.2.5.]

The mass spectra of PETriN, PEDiN and PEMN are shown in Fig. 4.2. The major ion for all compounds is the [M$^{+35}$Cl]$^-$ ion. The strong intensity of the chloride adduct is a result of the post-column addition of chloroform. When no post-column additive was used, a variety of adducts were formed. Stimulating the formation of a specific adduct, in this case the chloride adduct, enhances the sensitivity and robustness of the method [1,2,8,9]. In addition, all compounds show the fragment ion [M–NO$_2^{+}$H$^{+}$35Cl]$^-$. Formate- and acetate-adduct formation was also observed during LC–MS analysis of RDX and was attributed to impurities in the mobile phase [13]. Interestingly, the acetate and formate adducts were not observed in the mass spectrum of PETN. Instead, the mass spectrum of PETN was characterized by the presence of the nitrate
adduct ([M+NO₃]), which has previously been reported [7,8], and the deprotonated molecular ion ([M–H]).

All compounds partially lose one or more nitro groups in the ion source, yielding a fragment ion with the same exact mass as the molecular ion of its less-nitrated analogue. Therefore, it is important to have all compounds baseline separated using liquid chromatography. This is demonstrated in Fig. 4.3, which shows a chromatogram of a mixture of PETN, PETriN, PEDiN and PEMN, containing 1.25 ppm of each analyte. This chromatogram also shows the difference in response for all four compounds, with PETN clearly showing the lowest signal.

### 4.3.2 Calibration

Linearity was demonstrated for each compound between 0.1 ppm and 5 ppm, as shown in Fig. 4.4. However, since degraded PETN samples show very low concentrations of PETriN, PEDiN and PEMN, the calibration range for these compounds was adapted for accurate quantitation.

![Calibration curves for PETN, PETriN, PEDiN and PEMN in the range of 0.1 ppm to 5 ppm. LC–MS conditions as described in section 4.2.5.](image)

Quantitation of all compounds was performed using the [M+35Cl]⁻ ion. The lowest detected amounts for PETN, PETriN, PEDiN and PEMN were 3, 1.5, 1 and 1 ppb.
respectively. The lowest concentrations at which these compounds could be determined with a relative standard deviation (RSD) below 10% were 7.5, 3.8, 2.5 and 1.7 ppb respectively. Determination of limits of detection and quantitation (LOD and LOQ) is difficult in this case, because of the variations in sensitivity that were observed. In addition, extracted-ion chromatograms from the high-resolution MS data do not contain noise or background signals, which restricts the use of the general approach to determine the LOD and LOQ ($S/N > 3$ and $S/N > 10$, respectively).

With the use of simulated samples at different concentration levels, accuracy and precision of the calibration were evaluated. Table 4.1 shows that for all compounds the accuracy of the method is between 85.7% and 103.7%. The lowest accuracy is obtained for PETriN, PEDiN and PEMN at their lowest concentration levels, which are close to their respective limits of quantitation. It is also observed that the samples with the lowest concentrations yield the lowest precision. The precision for all compounds varies between 1.3% and 11.5% CV (coefficient of variation).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Accuracy (%)</th>
<th>Precision (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>low</td>
<td>med</td>
</tr>
<tr>
<td>PETN</td>
<td>103.7</td>
<td>102.0</td>
</tr>
<tr>
<td>PETriN</td>
<td>85.7</td>
<td>97.8</td>
</tr>
<tr>
<td>PEDiN</td>
<td>94.4</td>
<td>98.2</td>
</tr>
<tr>
<td>PEMN</td>
<td>92.2</td>
<td>99.4</td>
</tr>
</tbody>
</table>

4.3.3 Effect of mobile-phase composition

The effect of the mobile-phase composition on the ionization of the four nitrate esters was investigated using direct infusion. The compounds were added to the chloroform solution, which in turn was added post-column to the mobile phase. This was done for each compound separately, because of interference of fragment ions of the higher nitrate esters. The chloride adducts of all four compounds showed an increase in MS response with increasing methanol content of the mobile phase (Fig. 4.5). Higher ion
abundance of chloride adducts of several compounds when chloroform was mixed with methanol, compared to chloroform mixed with methanol/water was observed by Zhu and Cole [6]. For PETN, the abundance of the \([M-H]\) ion increased together with that of the \([M+^{35}Cl]\) ion, whereas the abundances of the nitrate adduct and of fragment ions decreased with increasing methanol content. The latter suggests that the nitrate-adduct formation originates from the fragmentation or decomposition of PETN itself. Similar processes were observed for PETN, NG and RDX by Tam and Hill [14] and Evans et al. [8], for ETN (erythritol tetranitrate) by Oxley et al. [5] and for RDX by Gapeev et al. [13]. Fragmentation and adduct formation were observed to decrease with increasing methanol/water ratios for the lower nitrate esters of PETN. The difference in response of the four compounds observed in Fig. 4.3 cannot be explained from the influence of the mobile-phase composition, because PETN elutes at the highest methanol/water ratio, where its response is higher than at lower methanol/water ratios.

\[ \text{Fig. 4.5.} \text{ Influence of the mobile-phase composition on the ionization of PETN, PETriN, PEDiN and PEMN. The intensity of the } [M+^{35}Cl]^- \text{ ion was normalized to } t=0 \text{ (10\% MeOH). Other conditions as described in section 4.2.5.} \]

**4.3.4 Relative response factors**

The previous chapter showed that peak-area ratios of a degraded PETN sample varied in time. This was likely a consequence of variations in the response factors of PETriN, PEDiN and PEMN relative to PETN. Using the custom-made standards, relative response factors were calculated using the slopes of the calibration curves (RRF = slope
analyte/slope PETN) during 34 series of experiments over a period of a year (Fig. 4.6). Significant variations were observed with minimum and maximum relative response factors, respectively, of 2.2 and 4.1 for PETriN, 4.1 and 8.7 for PEDiN, and 3.0 and 8.4 for PEMN. Coefficients of variation (CV) for the RRFs of PETriN, PEDiN and PEMN were 14%, 22% and 28%, respectively. The fact that the relative response factors can change by more than a factor of two underlines the necessity of using standards for accurate quantitation of PETriN, PEDiN and PEMN in degraded PETN samples. During the course of the measurements the observed variations (CV) in the absolute sensitivities were 29% for PETN, 23% for PETriN, 27% for PEDiN and 30% for PEMN. Since the variation in absolute sensitivity was comparable for all four compounds, the observed variations in RRFs could not be attributed to a variable sensitivity for one compound only.

![Graph](image)

**Fig. 4.6.** Variation in relative response factors (RRF) for PETriN, PEDiN and PEMN obtained during 34 series of experiments performed within a period of a year. LC–MS conditions as described in section 4.2.5.

### 4.3.5 Matrix effects

The matrix effects of acrylic textile, sterile gauzes (swabs) and soil were evaluated at two concentration levels, as shown in Table 4.2. For acrylic textile and swabs the recoveries for all compounds were between 89.9% and 103.4%. For soil, the recoveries of PEMN were 126.3% and 115.9% for the lower and higher concentrations, respectively.
PEMN is the first eluting compound from the LC column, and because of the gradient used, it is possible that water-soluble compounds from the soil co-elute with PEMN, resulting in ionization enhancement. The recovery of PEDiN, which is also an early-eluting compound, is also slightly enhanced (110%) at the lower concentration, whereas no matrix effects were observed for PETriN and PETN. The effect of soil matrix on the recoveries of PEDiN and PEMN seems to be less pronounced at higher concentrations of these compounds. Blank matrix extracts did not show any signals that correspond to the four compounds. Because of the large effect of a soil matrix on the quantification of PEMN, it is advised to use matrix-matched calibration curves in such cases.

Table 4.2. Matrix effects observed for PETN and its less-nitrated analogues. Shown in % recovery ± 1 standard deviation (n = 3).

<table>
<thead>
<tr>
<th></th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Swab (Acrylic)</td>
<td>Soil (acrylic)</td>
</tr>
<tr>
<td>PETN</td>
<td>102.5 ± 1.9</td>
<td>89.9 ± 4.5</td>
</tr>
<tr>
<td>PETriN</td>
<td>103.0 ± 5.8</td>
<td>101.5 ± 6.9</td>
</tr>
<tr>
<td>PEDiN</td>
<td>104.1 ± 7.5</td>
<td>101.0 ± 9.7</td>
</tr>
<tr>
<td>PEMN</td>
<td>103.4 ± 13.8</td>
<td>100.8 ± 15.3</td>
</tr>
</tbody>
</table>

4.3.6 Discrimination between post-explosion PETN and naturally-degraded PETN

In the previous chapter we investigated the possibility to discriminate between post-explosion PETN and naturally-degraded PETN, to investigate whether a suspect could have been present on a crime-scene. In the absence of standards of PETriN, PEDiN and PEMN, results were based on peak-area ratios. In the light of the large variations in relative response factors, the previous results should be re-evaluated. Naturally-degraded PETN samples were reanalyzed. These samples were prepared by storage of PETN on textile at 60°C for 12 weeks (the degradation experiments have been described in section 3.2.4). Due to the limited amount of material available after an explosion, the post-explosion samples could not be reanalyzed. Therefore, concentrations of PETriN, PEDiN and PEMN in the post-explosion samples were estimated using the relative response factors obtained using the custom-made standards. Based on the variation in
response factors observed in this study, the ratio in amounts relative to PETN as obtained from the post-explosion experiments ranged from 0.046 to 0.34 for PETriN, from 0.0038 to 0.14 for PEDiN and from 0.0002 to 0.093 for PEMN. The highest relative response factor of PETriN observed (4.1 vs. PETN) results in the lowest concentration ratios for the post-explosion samples. By using the ‘worst-case’ response factors, the difference between the two groups would be smallest. As shown in Fig. 4.7, the relative-frequency-density distributions of the PETriN/PETN ratios of naturally-degraded PETN and post-explosion PETN can still clearly be discriminated from each other. Two-sample t-testing shows that the difference between the two types of PETN is significant, with $t = 7.5$ and $p = 4.5 \times 10^{-6}$.

Although the use of the PEDiN and PEMN content in degraded PETN samples may increase the evidential value, combining the three ratios is not straightforward, since the formation of the three degradation products is not independent. In addition, the variation in the RRF of PETriN was lower than that for PEDiN and PEMN (14% CV vs. 22% and 28%, respectively). This renders the use of the PETriN/PETN ratio for discrimination between post-explosion PETN and naturally-degraded PETN more robust.

![Figure 4.7](image-url) **Fig. 4.7.** Relative-frequency-density distributions of the PETriN/PETN concentration ratio for naturally degraded PETN (60°C, 12 weeks) and post-explosion PETN. The relative-frequency density is the frequency normalized to the number of samples per group ($n = 12$ for natural degradation and $n = 14$ for post-explosion) and the bin size.
4.3.7 Application to PETN post-explosion case samples

To demonstrate the validity of using the custom-made standards to differentiate between post-explosion PETN and natural degradation of PETN under realistic circumstances, five post-explosion samples from NFI casework were analyzed with the developed method. In these selected cases PETN was identified as the main explosive involved using the LC–MS screening method of the NFI [15]. Case samples 1–4 originated from swabs of metal surfaces sampled after safe crackings and case sample 5 was a soil sample obtained after explosion of an intact device. The swabs and soil were extracted with methanol and concentrations of PETN, PETriN, PEDiN and PEMN were determined using the custom-made standards. In all samples PETN, PETriN, PEDiN and PEMN were identified. However, the levels of PETN, PEDiN and PEMN in case sample 3 were too low for quantification as well as the levels of PEDiN and PEMN in case sample 4. The levels of PETriN, PEDiN and PEMN relative to PETN for the case samples are shown in Table 4.3. Although the calculated PETriN/PETN ratios in the samples obtained from the post-explosion experiments were between 0.046 and 0.34, higher ratios were observed for case samples 1 and 2. The differences in ratios observed between the explosion experiments and the actual casework can be caused by many factors including charge, explosion conditions, sampling and time between explosion and crime-scene investigation. In general it can be stated that the explosion experiments were conducted under controlled conditions and with a relatively small explosive charge (15 g of PETN). The casework samples indicate that under realistic conditions the relative amount of PETN degradation products can be increased even further. This shows that differentiation in actual investigations is even stronger than was already demonstrated from the explosion experiments. Analyzing PETN post-explosion samples from future casework will enlarge the PETN post-explosion data set. This will allow accurate modeling of the relative-frequency-density distribution to determine the evidential value. Comparing the PETriN/PETN ratios in the post-explosion case samples to the PETriN/PETN ratios obtained for the natural degradation samples confirms that quantitation of PETN and its degradation products allows for discrimination between naturally-degraded PETN and post-explosion PETN.
Table 4.3. Concentrations of PETN and its degradation products in the methanol extracts of post-explosion PETN samples and the levels of degradation products relative to PETN.

<table>
<thead>
<tr>
<th></th>
<th>Concentration (ppb)</th>
<th>Levels rel. to PETN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PETN</td>
<td>PETriN</td>
</tr>
<tr>
<td>Case sample 1</td>
<td>7.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Case sample 2</td>
<td>54</td>
<td>58</td>
</tr>
<tr>
<td>Case sample 3</td>
<td>-</td>
<td>5.0</td>
</tr>
<tr>
<td>Case sample 4</td>
<td>28</td>
<td>4.8</td>
</tr>
<tr>
<td>Case sample 5</td>
<td>280</td>
<td>69</td>
</tr>
</tbody>
</table>

4.4 Conclusions

Using custom-made standards of PETriN, PEDiN and PEMN, which are common degradation products of the explosive PETN, a method for accurate calibration of these compounds was developed. Response factors of PETriN, PEDiN and PEMN relative to PETN were shown to vary by more than a factor of two over a period of a year, demonstrating the need for accurate calibration. Accuracy for all of the compounds was between 85.7% and 103.7%, with the lowest accuracies obtained for PETriN, PEDiN and PEMN at their lowest concentration levels, which are close to their respective limits of quantitation. Precision ranged between 1.3% and 11.5% CV.

This research also demonstrated that quantification of degradation products in degraded PETN can be used to discriminate between natural degradation and degradation by explosion. This information can be used when investigating a possible link between a suspect and a crime scene.
References