Method development for trace analysis of emulsion and peroxide-based explosives by headspace GC/MS and CE/DAD

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Abstract

Organic peroxide explosives have become more popular in terrorist attacks fairly recently. It is important that security institutions and authorities have capabilities to investigate such incidents and analyse these compounds. However, chemical analysis of organic peroxides is not quite simple. High susceptibility to elevated temperatures makes their analysis complicated.

In this work, suitability of a gas chromatographic method combined with mass spectrometry and headspace sampling for the analysis of peroxide-based explosives was studied. A capillary electrophoresis method using MEKC technique and optical detection was also tried for this purpose. Besides the organic peroxides, capabilities of the HS/GC/MS method was also experimented for analysis of emulsion explosives.

Objective of this thesis was to develop methods for the purposes described above, and to optimise their parameters. All steps of the analysis from the beginning to the end were studied in the method development phase. Performance parameters, such as limit of detection and ruggedness, were also determined.

A viable trace analysis method for TATP was successfully developed with the GC/MS. For other peroxides and emulsion explosives, equally good analytical results were not achieved. Further validation and experiments are needed to extend the scope of the method to their analysis. Analysis of organic peroxides with given capillary electrophoresis instrument and buffer solutions requires further method development, due to low sensitivity.

Keywords Peroxide-based explosives, emulsion explosives, trace analysis, chromatography, capillary electrophoresis

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Tiivistelmä

Orgaanisten peroksidiräjähteiden käyttö terrori-iskuissa on yleistynyt melko hiljattain. Turvallisuusviranomaisten on tärkeää kyetä tutkimaan kyseisenlaisia iskuja ja tunnistamaan näitä yhdisteitä. Orgaanisten peroksidiräjähteiden kemiallinen analytiikka ei kuitenkaan ole aivan ongelmatonta. Niiden lämpöherkkyys monimutkaistaa niiden analysointia merkittävästi.

Tässä työssä tutkittiin kaasukromatografia-massaspektrometrisen menetelmän soveltuvuutta orgaanisten peroksidiräjähteiden määrittämiseen headspace-näytteenotolla. Samaan tarkoitukseen testattiin myös kapillaarielektroforeesimenetelmän soveltuvuutta optisella detektiolla MEKC-menettelyllä. Orgaanisten peroksidien lisäksi HS/GC/MS-menetelmän soveltuvuutta kokeiltiin emulsioräjähteille.

Työn tavoitteena oli kehittää analyysimenetelmät edelläkuvattuihin tarkoituksiin, ja optimoida niihin liittyvät parametrit. Menetelmäkehityksessä tarkasteltiin analyysin kaikkia vaiheita. Menetelmille määritettiin tulosten perusteella laadulliset parametrit, kuten toteamisraja sekä häiriönsietokyky.

Orgaanisista peroksideista TATP:lle onnistuttiin kehittämään toimiva headspace-jäämäanalyysimenetelmä GC/MS-laitteella. Muiden peroksidien ja emulsioräjähteiden osalta yhtä hyviin analyysituloksiin ei päästy. Menetelmän laajentamiseksi näiden analysointiin tarvitaan lisävalidointia ja -tutkimuksia. Orgaanisten peroksidien analysointi testatulla kapillaarielektroforeesilaitteistolla ja ajopuskuriliuoksilla vaatii menetelmän jatkokehitystä, todetun alhaisen herkkyyden vuoksi.

Avainsanat Orgaaniset peroksidiräjähteet, emulsioräjähteet, jäämäanalyysi, kromatografia, kapillaarielektroforeesi

Contents

Symbols and abbreviations

Symbols

A_{peak}	Area of a peak
$I_{\mathrm{peak}}/I_{\mathrm{max}}$	Relative height of a peak compared to the highest peak
I_{peak}	Peak height
l_{Twister}	Length of a Twister SBSE sorbent rod
Q_{TCF}	Transfer column flow
T_{aux}	Mass spectrometer transfer line temperature
$T_{\mathrm{cryo,high}}$	Releasing temperature of the cryogenic trap
$T_{\mathrm{cryo,low}}$	Trapping temperature of the cryogenic trap
T_{HS}	Headspace sample collection temperature
t_{HS}	Headspace sample collection time
T_{inlet}	Inlet temperature
$T_{\mathrm{oven,final}}$	Final temperature of the column oven
$T_{\mathrm{oven,initial}}$	Initial temperature of the column oven
t_{RT}	Retention time
T_{TD}	Thermodesorption temperature of the instrument inlet
t_{TD}	Thermodesorption time
$T\ t_{\mathrm{oven}}^{-1}$	Column oven heating ramp rate
V_{HS}	Headspace sample container volume
V_{inj}	Sample injection volume

Abbreviations

AN	Ammonium nitrate
CE	Capillary electrophoresis
DAD	Diode array detector
EOF	Electro-osmotic flow
FO	Fuel oil
GC	Gas chromatography
HMTD	Hexamethylene triperoxide diamine
HS	Headspace
LC	Liquid chromatography
MEKP	Methyl ethyl ketone peroxide
MS	Mass spectrometry
PDMS	Polydimethylsiloxane
SBSE	Stir bar sorptive extraction
SDS	Sodium dodecyl sulphate
SPME	Solid phase micro extraction
TATP	Triacetone triperoxide

1 Introduction

Organic peroxide explosives have become relatively popular in terrorist attacks in the recent decades [1]. Main motives for such transition are the ease of synthesis of peroxide explosives and the availability of their precursor materials [2]. Physicochemical properties of organic peroxides, such as volatility, thermolability and instability, pose challenges to traditional analytical methods to identify these compounds. Thus, one of the topics of this thesis is the development and optimisation of methods for the analysis of organic peroxides by gas chromatography mass spectrometry (GC/MS) and capillary electrophoresis with diode array detector (CE/DAD).

Another goal of this thesis was to determine whether a GC/MS technique with headspace sampling would be suitable for detecting emulsion explosives. Emulsion explosives consist mainly of ammonium nitrate, water, stabilisers and hydrocarbon components [3]. Simultaneous presence of organic and inorganic components in emulsion explosives in turn sets challenges to their analysis. Hypothesis is that the headspace extraction would be capable of evaporating the hydrocarbon component and thus allow its collection by sorptive enrichment and analysis by GC/MS.

Adapting to changing modes of hostile activities is a high priority to law enforcing and national security agencies. To keep track of developments of possible terrorist attack methods, it is necessary for the authorities to update their existing analytical methods and launch new ones. In the event of a deliberate ill-intended explosion, law enforcement agencies must have capabilities to identify and prove what type of blasting agent was used. This identification can be a key part of evidence and can be used to direct investigation and possibly narrow down the group of suspects.

Typical samples from an explosion incident scene are debris from the surroundings. Materials of such samples typically consists of debris of constructed environment such as metal, glass, stone, plastic and wood. The size of such samples might become a problem from the viewpoint of chemical analysis. It might be difficult to pinpoint items from the crime scene that would most probably have explosive residues on them. Consequently, a larger bulk of sample material might have to be recovered. The downside is that large samples are usually difficult to process in a laboratory in terms of sampling.

Headspace extraction with sorbent enrichment is a widely used sampling method for GC analyses, especially when samples are large in size and analytes are sufficiently volatile. With headspace sampling, samples might not require any extraneous processing other than heating with a selected sorbent material that collects the evaporated analyte compounds. Sample introduction into the analytical instrument with sorbent enrichment is equally easy, as thermodesorption does not require any other steps than heating the sorbent material. Headspace sampling can save time and effort, compared to liquid extractions that may involve plenty of extra steps in addition to handling and disposing of solvents. Liquid extracts might also require filtration, chemical modification and concentrating, all of which processes demand additional work, time and materials. Also, headspace sampling is especially suitable for large samples.

Forensic laboratory of National Bureau of Investigation, to which this thesis was done for, already had a GC/MS instrument with a multimode inlet in use. The aim of this method development was to test and demonstrate the suitability of the instrument for the intended purposes. After proving viability of the concept, the aim was to also find the optimal parameters to facilitate the analyses. Organic peroxide analyses were also performed on a capillary electrophoresis instrument already in use in the laboratory, using a micellar electrokinetic chromatography (MEKC) technique. Advantage of the CE technique over GC is the working medium of the instrument. Capillary electrophoresis works in a liquid phase and thus involves much lower analysis temperatures than GC, which is a clear benefit when working with thermally unstable samples.

The three peroxide explosives, that that were studied in this thesis, were: triacetone triperoxide (TATP), hexamethylene triperoxide diamine (HMTD) and methyl ethyl ketone peroxide (MEKP). Each of the peroxides have different properties, both physical and chemical, for which reason simultaneous analysis for all of them is challenging. Of the peroxides, TATP is highly volatile, and thus is favorable for headspace sampling and the GC/MS technique. In turn, HMTD has a very low vapor pressure and is barely volatile and is thermally unstable. These properties make it difficult to be analysed with headspace sampling and to be analysed with the GC/MS. Headspace sampling of the peroxides was done by using PDMS coated sorbent rods and a manual SPME fibre assembly.

A method capable of analysing emulsion explosives as a whole seems unlikely. Individual components of the emulsion explosives are easy to analyse, but simultaneous analysis of hydrocarbons and inorganic ammonium nitrate does not fit well to traditional methods. For this reason, it is logical to employ GC/MS for the hydrocarbon component and for example CE/DAD for the inorganic component.

2 Literature review

In this chapter, properties of organic peroxide explosives and emulsion explosives are examined. Also, existing analytical methods for their analysis are reviewed. Finally, aspects of gas chromatography and capillary electrophoresis as analytical techniques are being discussed.

2.1 Organic peroxide explosives

In general, organic peroxide explosives are energetic materials that contain a peroxide functional group (R–O–O–R) in their structure [4, p. 30]. In most cases, the reactivity of organic peroxides is a consequence of oxygen's high electronegativity, and in some cases because of high bond strain [5]. The bond dissociation energy of an organic peroxide bond (R–O–O–R) is approximately at 150 – 170 kJ/mol range, whereas the bond dissociation energy for typical peroxide decomposition products are at 500 kJ/mol range [6, p. 313]. Because of the large difference in bond energies, the decomposition process of organic peroxide compounds is highly exergonic. However, it is noteworthy that there are speculations based on computational models that the decomposition reaction of organic peroxides is not thermochemically highly favored reaction, but rather that the energetic nature of the process would be a result of an entropy burst [7].

A well-known property of the organic peroxides is their instability. As primary explosives, organic peroxides can be initiated to explode by friction, heat or mechanical shock [8]. This property renders them essentially useless for legitimate applications and makes their handling and synthesis exceptionally dangerous. However, their sensitivity can be seen as a benefit for illicit uses, as they can be easily detonated with simple equipment and disarming of such devices is dangerous and undesirable. Especially three organic peroxides are under a special interest of terrorists. These three peroxides are introduced next.

2.1.1 Triacetone triperoxide

Triacetone triperoxide (TATP) is one of the most commonly used improvised explosives in malicious acts. The structure of TATP contains three acetone molecules joined together in a ring structure with peroxide bonds. Its chemical structure is shown in Figure 1. At room temperature TATP exists as a white powder or in white crystalline form. Synthesis process of acetone peroxide yields a mixture of two different forms of the organic peroxide [9]. These products are TATP and diacetone diperoxide, also called DADP. The DADP has practically the same properties as TATP, so the focus in this thesis will be on TATP.

The popularity of TATP in terrorist attacks can be mostly explained by its easy synthesis. Materials and precursors required to make TATP are quite common and readily available. The main ingredients needed for TATP synthesis are acetone, hydrogen peroxide and an acid. Acetone is a common solvent and is used widely in many different industrial branches. In many countries, there are no buying restrictions

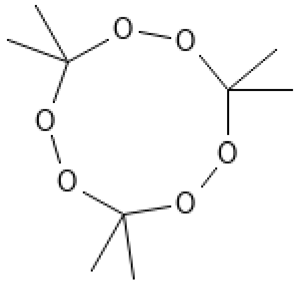


Figure 1: Chemical structure of TATP

on acetone and it can be usually bought from hardware stores. While there are no buying restrictions on acetone, consumers in the European Union can only buy hydrogen peroxide to a limited extent in terms of concentration. In the EU, a license is required to buy hydrogen peroxide above certain threshold concentration. In Finland, consumers can apply for a license to buy hydrogen peroxide at 12 – 35 mass percent region. Licenses are permitted by local law enforcement offices. Also, the European Union has set restrictions on buying some of the concentrated strong acids. Among other reasons, these actions have been taken as an effort to make acquiring of the precursors of the organic peroxides more difficult.

Synthesis of TATP is performed as an acid-catalysed reaction of acetone and hydrogen peroxide [10]. One of the most typical synthesis methods is to first mix medium concentration hydrogen peroxide and acetone. Then cooling the mixture in an ice water bath and slowly start adding the acid under stirring. After the acid addition, the reaction mixture is taken out off the ice water bath and is left to sit in room temperature for 24 hours. During the waiting phase, TATP crystallises from the mixture. Finally, the crystals are filtered out of the reaction mixture and washed thoroughly with water. [11]

The explosion mechanism of TATP is a type of a decomposition reaction. Instead of rapid redox reaction, which is the typical reaction method of explosives, decomposition does not necessarily involve large release of thermal energy. One proposed decomposition route of a TATP molecule is shown in Figure 2. It can be seen, how dissociation of TATP occurs due to bond cleavages. Destruction power of a decomposition reaction is a consequence of formation of gaseous products from solid reactants, which causes a large increase in volume and pressure to the surroundings. This mechanism is essentially the same for traditional explosives, but in contrast, the explosion of traditional explosives is also strongly exothermic.

The vapor pressure of TATP has been reported to be 6.39 – 7.87 Pa at 25 °C [12], [13]. Due to its high vapour pressure, it readily sublimes at room temperature. To put the vapor pressure in perspective, TATP will lose approximately 66 % of its mass within 2 weeks at room temperature [7]. There has been extensive research done to determine the thermal stability properties of TATP. Its thermal decomposition reaction has been found to be of first order reaction kinetics and the reaction rate has been found to be linear with temperature, with a reaction rate coefficient approximately $6.84 \cdot 10^{-6}$ s^{-1} at 151 °C [12], [14]. By its explosive performance,

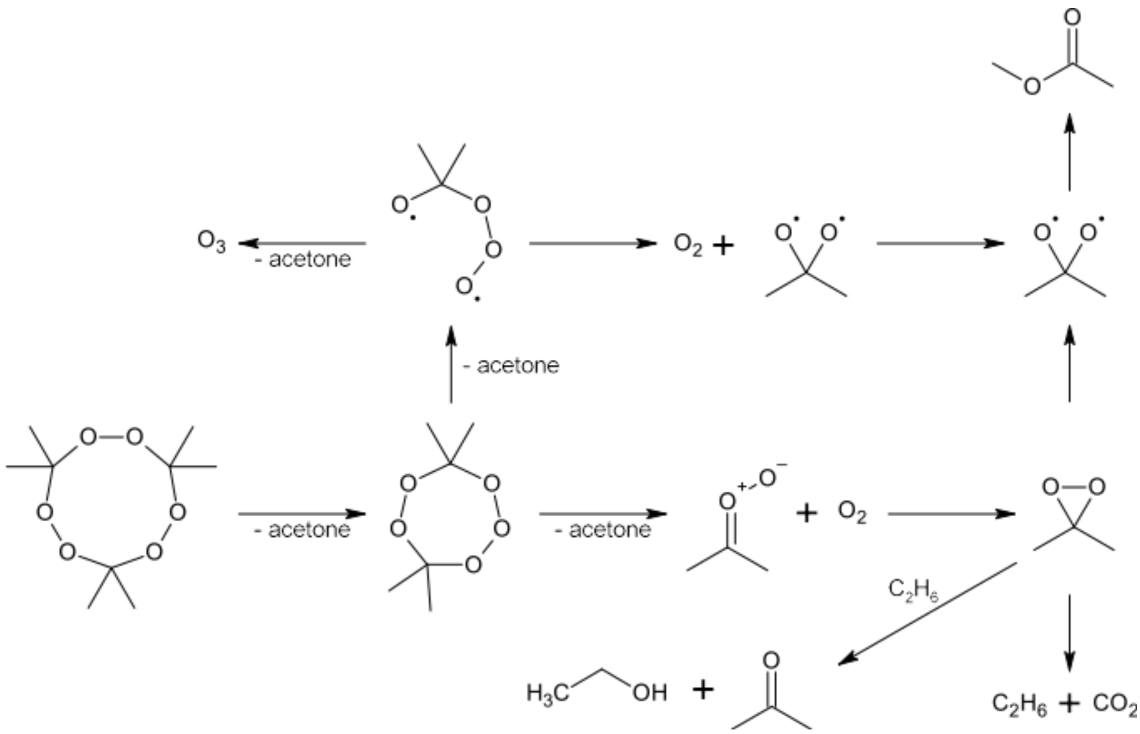


Figure 2: Suggested decomposition route of TATP (simplified) [7]

TATP somewhat equals with TNT [7]. However, due to the low density of TATP, more of it is needed in terms of volume to produce same effect as TNT. The low density is also reflected in other performance parameters, making it inferior explosive compared to actual, useful secondary explosives. [15] Nonetheless, TATP still is lucrative substance for terrorists due to its damaging capabilities, and especially: easy synthesis.

Many research papers and method development reports have been published describing trace analysis techniques of TATP. A common method used for this purpose is liquid chromatography with mass selective detector (LC/MS) [16]. Several publications describing feasibility and performance of LC/MS methods for the purpose can be found. LODs as low as 10 ng have been reported for these techniques [17]. Other common techniques are HS/GC/MS, direct analysis in real-time mass spectrometry (DART-MS) and capillary electrophoresis (CE) [18], [19], [20]. Of these methods, LC/MS has the lowest LOD and DART-MS seems to have the least laborious sample treatment.

Numerous terrorist attack cases are known that involve the use of TATP. One of the most notable ones being the November 2015 Paris attacks in France, an incident involving loss of 132 lives. Another notorious case being Brussels bombing in 2016, an incident involving loss of 35 lives. One of the latest incidents involving the use of TATP is the 2017 Manchester bombing, an incident involving loss of 23 lives. It is quite remarkable that TATP as an explosive material in terrorist attacks have only began emerging over the recent years and decades. [21]

2.1.2 Hexamethylene triperoxide diamine

Hexamethylene triperoxide diamine (HMTD) is a primary explosive which consists of nitrogen, hydrogen, oxygen and carbon. HMTD, as its name suggests, has three peroxide bonds and it has a cage-like structure, as shown in Figure 3. Similar to TATP, it is also sensitive to shock, friction and heat but slightly less than TATP. Also similarly to TATP, HMTD exists as a white powdery substance at room temperature. It has no commercial or practical uses due to its instability.

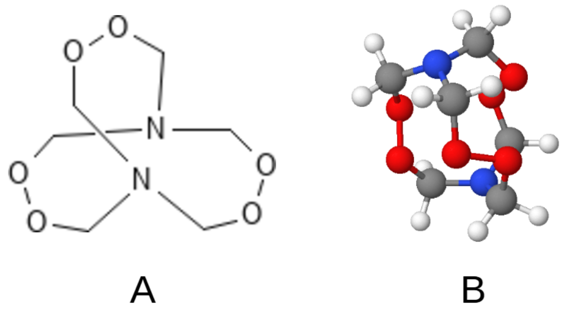


Figure 3: Chemical structure of HMTD (*A*: condensed formula of HMTD, *B*: ball-and-stick model of HMTD)

Like TATP, HMTD has also been used in terrorist attacks as an explosive material. Materials needed for the synthesis of HMTD can be easily acquired from common sources. Typical synthesis path of HMTD is through acid-catalysed reaction between hydrogen peroxide and hexamethylenetetramine, also known as hexamine. Hexamine for this purpose is typically extracted from cooking stove fuel tablets used for camping. Other than that, the synthesis procedure of HMTD is quite similar to that of TATP [22].

A significant difference of HMTD compared to TATP is its vapor pressure, which is much lower for HMTD. According to Aernecke *et al.* the vapor pressure of HMTD at 20 °C is $4.5 - 6.1 \cdot 10^{-6}$ Pa [23]. Compared to the vapor pressure of TATP ($6.39 - 7.87$ Pa at 25 °C). The vapor pressure is a very important parameter when working with headspace sampling. If a sample compound is not volatile enough, it does not transfer adequately into the vapor phase and thus cannot be collected with sorbent enrichment or other headspace sample recovery methods. Thus, the low vapor pressure of HMTD is quite an important feature to consider.

According to simulations, the TNT equivalency of HMTD is slightly lower than that of TATP. Simulated TNT equivalency of HMTD is reported to be 0.82, and in comparison: 0.92 for TATP [24]. Calculated TNT equivalency of HMTD has been found to be slightly lower than the simulated equivalency: 0.74, and 0.80 for TATP [25]. Thermal stability of HMTD is much worse than that of TATP [26, p. 16]. Thermal decomposition reaction of HMTD has been suggested to be of first order reaction kinetics [22]. Its reaction rate has been found to be linear with temperature, with a reaction rate coefficient approximately $1.78 \cdot 10^{-3}$ s^{-1} at 151 °C [12].

Analysis of HMTD is notoriously challenging. Nonetheless, many scientific publications are available describing its analysis with a variety of different techniques.

There has been many reported cases of challenges with the thermal instability of HMTD [12], [27]. However, some have reported successful headspace analysis of HMTD with GC/MS [28]. Also, analysis of HMTD by decomposition products have been reported [29]. Like for TATP, many LC/MS methods have been reported for HMTD [17], [30].

There are also several known cases of HMTD being used as an explosive in terrorist attacks. A very significant case in which HMTD was used was the 2016 New York bombing, in which HMTD was used as a detonator, triggered by a phone and electricity [31]. Another significant attempt to use HMTD for malicious purposes was the December 1999 Los Angeles airport plot, where the peroxide was intended to be used, but the attempt was pre-emptively foiled by the officials [32], [33, pp. 486–487].

2.1.3 Methyl ethyl ketone peroxide

Methyl ethyl ketone peroxide (MEKP) is a peroxide compound that consists of two or more methyl ethyl ketone molecules joined together by a peroxide bond. Chemical structure of MEKP is presented in Figure 4. Likewise TATP and HMTD, MEKP is an unstable organic peroxide. However, unlike the two other peroxides, MEKP is an oily liquid at room temperature and it has commercial use. MEKP is used as a curing agent in polymer industry, especially for polyester resins [34, p. 458].

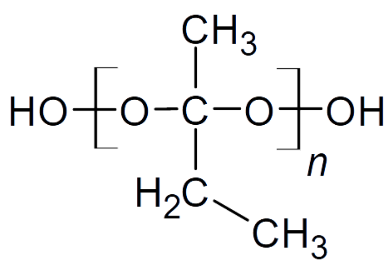


Figure 4: Chemical structure of MEKP, n denotes varying integer number of MEK monomers in MEKP chain

In industrial scale, MEKP is typically produced by slowly adding acidified hydrogen peroxide solution into methyl ethyl ketone under vigorous stirring [35]. As a commercial product mixed with phlegmatisers, its flash point is 56 °C [36]. Thus, it is suitable for GC analysis. However, it also starts to decompose at 60 °C [36]. MEKP is available commercially as a chemical, typically used in polymer manufacturing. MEKP is sold only as a mixture of phlegmatisers, which typically are phtalates [37, p. 11].

Decomposition of methyl ethyl ketone peroxide can occur via three different pathways. First of these is a radical decomposition, which is initiated by heat or absorption of light. Free radicals are formed of the peroxide molecules which react with more peroxide molecules and cause an increase in heat. A feedback loop is created and a thermal runaway is possible. Another type is redox decomposition, which is initiated by electron exchange redox reactions with metals. As a product, free radicals are once again being formed. The third type is acid decomposition, which in turn is initiated by the presence of an acid. Free hydrogen ions trigger a reaction chain producing peracetic acid and ethanol. These products can again react with MEKP molecules and create a feedback loop and cause a thermal runaway. [38]

The characteristics of the decomposition process of MEKP depend on the ratio of amounts between the monomer and the different oligomers of the peroxide. Especially large abundance of the dimer species in formulation of the peroxide will lower the onset temperature of the mixture [38]. In other words, the more there is of the dimer species of MEKP present in the mixture, the lower the thermal runaway initiation temperature.

Available information and research of GC analysis of MEKP seems to be quite scarce. Only a few descriptions of such analytical application can be found. Nnaji *et al.* have reported of successful GC/MS analysis of MEKP, however [39]. Instead, methods based on liquid chromatography seem to be more popular, even though, GC can still be a viable tool for such analyses [40], [41].

Terror incidents involving the use of MEKP as an explosive material are quite rare. Methyl ethyl ketone peroxide is relatively inconvenient to be used as an explosive, mainly due to its extreme sensitivity to heat. Moreover, the availability of commercial MEKP is limited and its synthesis by improvised equipment is particularly difficult without causing an accidental explosion. Besides all, if MEKP was to be synthesised at home, one should also acquire suitable desensitising agents in order to make the handling of the peroxide practical in any way. Thus, the two other organic peroxide explosives are quite a bit more luring for illicit uses.

It should be noted though, that MEKP has been involved in numerous accidents where a thermal runaway has occurred and lead to an explosion [38]. These accidents have taken place in industrial settings and under certain conditions. There is very little information of MEKP being used in terrorist purposes, as has also been noted in literature [26, p. 20]. However, there are still concerns that it is a potential material for improvised explosive devices (IEDs) and should be therefore considered a risk in the future too.

2.2 Emulsion explosives

Emulsion explosives are a type of explosives that are commonly used in mining. Main ingredients of emulsion explosives are hydrocarbon fuel, aqueous solution of oxidiser salts (typically ammonium nitrate), a density modifier, an emulsifying agent and a small amount of additives [42, pp. 419–420]. By their ingredients, emulsion explosives are quite close to traditional ammonium nitrate fuel oil (ANFO) explosives. As the name implies, ANFO consists of ammonium nitrate (AN) and fuel oil (FO). The big difference between these two explosive types is that emulsion explosives are water resistant, whereas ANFO cannot be used in mining settings where water is present in the boreholes or the conditions are otherwise wet [43].

The water resistance feature of emulsion explosives is a consequence of an emulsifying process, that lends the name to this group of explosives. More accurately, emulsion explosives are so-called water-in-oil emulsions. This means that the aqueous oxidiser solution forms microscopic micelles, or bubbles, that are being suspended in the continuous hydrocarbon fuel phase [44, p. 384]. The hydrophobic fuel component prohibits water coming in contact with the oxidiser and thus dissolving it. ANFO, in turn, is made by simply mixing ammonium nitrate and fuel oil in 94 % to 6 % ratio, respectively [3, p. 282]. Emulsion explosives manufacturing, however, requires extra steps.

The emulsifying treatment of emulsion explosives can be done with multiple different chemicals. These chemicals vary from different fatty acid salts to non-charged esters [42, p. 420]. Naturally, all chemicals used for this purpose are surfactants, which allow the formation of micelles in the water-in-oil emulsion.

Emulsion explosives must be sensitised before use, in order them to have explosive properties or initiation sensitivity. The sensitisation is done by decreasing the density of the bulk material. This process can be done by gassing the mixture under vigorous stirring or by adding very small hollow balloons made of plastic or glass into it. [42, p. 420] These pores act as initiation sites when the matrix is being detonated. The voids collapse creating adiabatic rise in temperature and initiating the reaction between the fuel and the oxidiser. [45] As this reaction occurs throughout the matrix, the detonation happens uniformally and the whole of the bulk material can be effectively used.

Ammonium nitrate serves as an oxidiser and as a heat producer in AN containing explosives. Hydrocarbons act as fuel that the oxidiser is oxidising. [3, pp. 281–282] Fuels in emulsion explosives can consist of various different organic fuels, such as mineral fuel oil, waxes or a mixture of these. The most typical varieties of these are diesel fuel and paraffin wax. [42, p. 419], [46]

The great benefits of emulsion explosives compared to the other types of blasting agents are: low-cost raw materials, non-sensitivity (i.e. safe to handle), versatility (ready-to-use packaged products and pumped products) and, in particular, water resistance. These properties make it quite logical why emulsion explosives have gained popularity in the mining industry.

2.3 Gas chromatography mass spectrometry

Gas chromatography has been used as a separation method for a long time and it has a well established role in analytical chemistry. A basic requirement for analytes to be suitable for GC analysis is that they must be volatile, or at least have high enough vapor pressure in the temperature range of the instrument, so that they can be evaporated. Other than that, GC is a very versatile separation method and can provide extremely good separation of numerous compounds.

Mass spectrometry is a widely used technique with many analytical applications. A very common application of it is being coupled to a another analytical instrument, typically a chromatograph or some other separating instrument. Besides working solely as a signal inducing appliance after a separating instrument, mass spectrometer provides characteristic information of compounds in the form of mass spectra. Certain ionisation methods with MS can provide very detailed information about the sample compounds. For example, electron ionisation (EI) causes compounds to fragment in certain patterns, that are nearly unique to each compound. From this information, the composition of the analytes can be deducted. This kind of information combined with repeatable time separation data, acquired from the separation methods, can be seen as some of the most versatile analytical methods for known and unknown samples.

A standard GC/MS method has several parameters that affect the analytical performance of a method. Due to the very nature of gas chromatography, many parts of the instrument operate at elevated temperatures. This property of the analytical technique can pose challenges when working with thermally unstable samples such as organic peroxides. Also, method development with such complex systems is not always straightforward. The number of parameters, and different combinations of them, affecting the analyses can be enormous. Especially when coupled with a multimode inlet and a mass spectrometer, the amount of analytical method parameters is vast.

Nowadays, the number of different sample introduction methods for GC is countless. These methods range from traditional liquid injection to complex on-line supercritical fluid sample extraction systems with cold trap focusing [47]. One traditional sampling, and sample introduction, method is the headspace sampling. Even headspace sampling alone features a large number of different variations. In general, headspace sampling can be divided into two main groups: static and dynamic [48, p. 251].

Static headspace extraction (SHE) is, in simple terms, a method where a sample (solid or liquid) is enclosed into a gas-tight vessel with a relatively small overhead gas volume. The vessel is then usually heated, typically in an laboratory oven. The principle is that volatile compounds evaporate and transfer as gases into the gas phase inside the vessel. After a sufficient period of time, the volatile compounds form an equilibrium, where evaporation of more sample molecules into the gas phase stops. After a specified time of heating, a small sample of the gas phase from the vessel is then recovered and introduced into an analytical instrument. [48, pp. 253–255].

Sample collection from the headspace volume can be done, for example, with a gas-tight needle or with sorbent enrichment methods such as solid phase micro extraction (SPME). The gas-tight needle method only takes an aliquot of the whole headspace volume and the concentration of a specific analyte equals the concentration of it in the headspace equilibrium. In contrast, sorptive sample collection methods (e.g. SPME) might be specific to some chemical properties of certain samples and only recover those from the headspace volume, without retaining others. This leads to a situation where sorptive methods may enrich certain compounds, as their adsorption from the gas phase to the sorptive matrix allows their further evaporation from the sample matrix into the headspace volume. However, the analytes also form an equilibrium with the gas phase off of the sorptive matrix, as the sorptive material is being held in the heaspace volume for the whole heating period. This phemomenon is being exploited typically in the sample introduction with sorbent enrichment methods, as the analytes are being released from the matrix with thermodesorption. The phase equilibrium of the SHE sorbent methods is illustratively described by Sithersingh and Snow, as shown in Figure 5. [48, pp. 253–257]

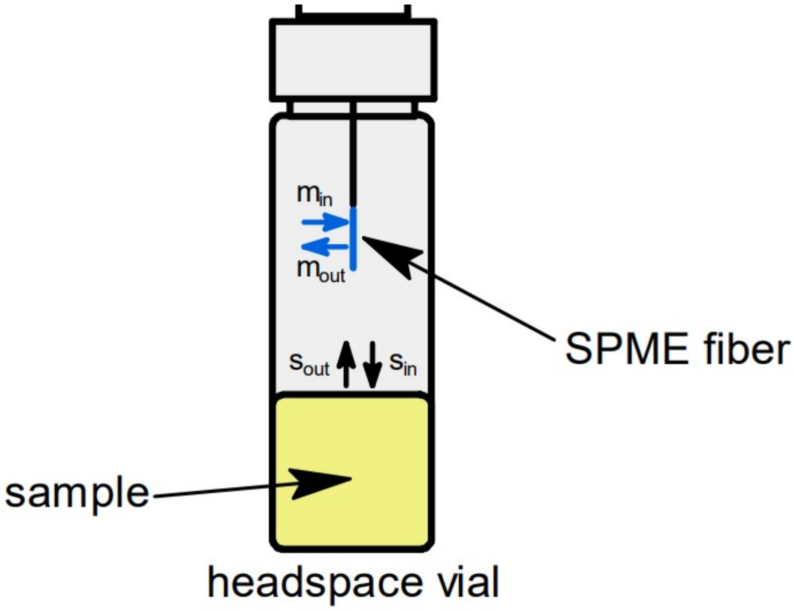


Figure 5: Headspace equilibrium between the phases in SPME fiber, m_{in} refers to the analyte adsorption into the sorptive matrix, m_{out} refers to the analyte evaporation out of the sorptive matrix, s_{out} refers to the analyte evaporation out of the sample matrix and s_{in} refers to the analyte dissolution/adsorption back into the sample matrix [48, p. 256]

Another type of static headspace sample collection method is the so-called stir bar sorptive extraction (SBSE). It is similar to SPME, but has significantly bulkier sorbent matrix phase. The SBSE sampling rods are basically magnetic stir bars enclosed in a glass capsule, which is coated with a sorbent material film. SBSE sampling rods are meant for analyte extractions from liquids by stirring or for headspace sampling from gas phases. Sample introduction with SBSE sorbent rods is performed by thermodesorption. [48, pp. 255–257]

Dynamic headspace extraction (DHE) differs quite substantially from the static type. In DHE, sample is placed inside a gas-tight vessel and a flow of pure, inert analytical gas is then directed into the container. Consequent outflow of the gas is then directed through a sorptive porous matrix, typically placed inside a tube, that adsorbs the analytes. Finally, after the aforementioned purge and trap phase, the sorbent tube is then used to introduce the sample into the analytical instrument, usually by thermodesorption. [48, p. 257] Only static headspace techniques were used for the experiments of this thesis, and thus DHE will not be discussed further.

Generally in gas chromatography, temperature of the injection port should be at least above the boiling point of the highest boiling analyte. For this reason, a common convention is to set the temperature of the inlet about $20 - 30$ °C above the highest temperature program temperature of the analytical column. [49] By doing so, accumulation of unwanted deposits of high-boiling contaminates to the inlet can be effectively avoided. However, heat of the injection port can cause thermal decomposition of thermolabile analytes. As a consequence, thermolabile compounds can already start to degrade at the beginning of the separation. Thermal degradation during instrumental separation typically causes broad peaks, peaks dividing into multiple ones (as the degradation products form their own peaks) or total disappearance of peaks. [50]

Typical observation for analytes that have already degraded in the inlet of the instrument, is the splitting of the parent peak into multiple ones and their elution earlier than when the parent peak would had eluted. Peak broadening and reduction in intensity might suggest thermal degradation occurring in the column, as different mass and size fragments are being created and they elute around the retention time of the parent peak. Finally, it is possible that an analyte degrades to a such extent, that the produced fragments have no retention to the analytical column and they exit the system very rapidly. Additionally, it is possible that the detector is not capable of detecting such small molecules, such as carbon dioxide or water. In this case, no peaks will be seen in the chromatogram. The different types of thermal degradation are illustrated in Figure 6. [50]

Organic molecules exhibit different thermal degradation pathways depending on the chemical structure, temperature, time of exposure to the hostile environment and the presence of degradation catalysers, among others. Organic molecules that contain nitrogen, sulphur, phosphorus or oxygen are especially susceptible to thermal degradation, as these functional groups might lower bond strengths in organic compounds. Different pathways of thermal degradation include: rearrangements, loss of functional groups, combinations and cleavages. Even active surfaces such as metal or glass might speed up decomposition of unstable molecules during a chromatographic analysis. For this reason, inert consumables for instrumental analyses have been introduced (e.g. inert liners and columns). [50], [51]

Mass spectrometry is an analytical technique that has a vast number of different variations. The principle and purpose of mass spectrometry is the detection and characterisation of chemical compounds. The key aspects of mass spectrometry in case of organic analyte are:

- sample introduction into the MS instrument
- ionisation of the samples
- filtering of different mass fragments of the samples
- detection of the analyte fragments

All of the different aspects listed above include a great number of different techniques, ranging from direction insertion probe sample introduction to liquid chromatography and detection methods from electron multiplier tubes to Fourier-transform ion cyclotron resonance detectors. This thesis focuses on electron ionisation (EI) single quadrupole (Q) spectrometer with an electron multiplier tube detector (EM), which is perhaps the most common type of MS instrument in use.

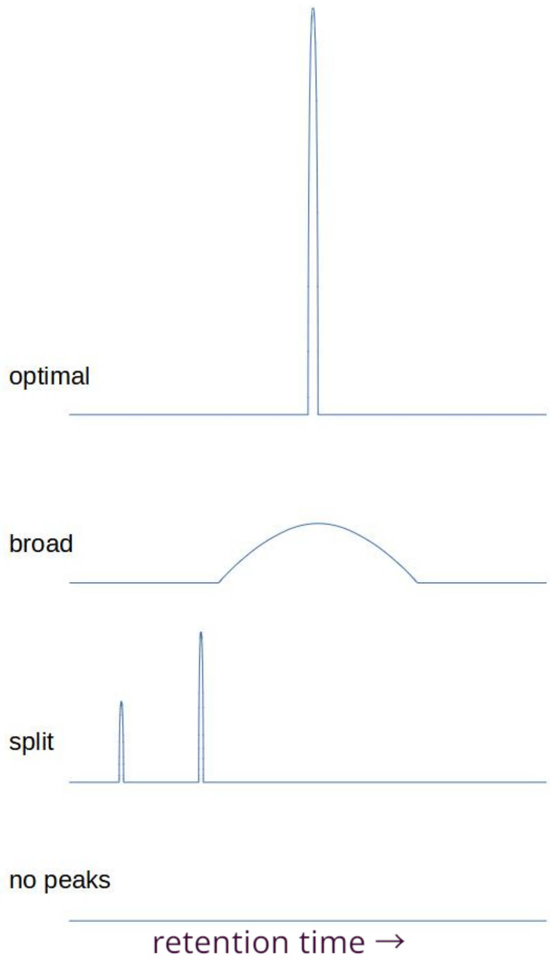


Figure 6: Different thermal degradation end results in GC chromatograms compared to the optimal analyte elution (optimal separation exhibits sharp, high intensity peak that is symmetrical and narrow) [50]

An EI-Q-EM mass spectrometer can provide valuable analytical data while being relatively simple, easy-to-use and a fairly low-cost method. Electron ionisation is possibly the most common ionisation technique among GC/MS instrument combinations. Electron ionisation produces fragments of molecules and ions in reproducible manner. Different fragmentation mechanisms are well known and they are listed in Table 1. Though, many more mechanisms still exist in addition to those listed in the previous table. Typically, mass spectrum libraries and tables of different mass fragments are used to interpret mass spectra of unknown samples and to verify findings of known sample components. Fragmentation types can be in turn used to predict mass spectra of organic compounds and to prove existence of certain molecules in a sample.

Table 1: Main fragmentation types of organic molecules in regards of electron ionisation MS

fragmentation type	typical fragment masses (m/z)	reference
sigma-bond cleavage (alkanes)	$\sum_{n=0}^{x-2} M[\mathrm{C_xH_{2x+2}}] - n \cdot 14$ (for n-alkanes), 83 (alkyl cycloalkanes)	[52, p. 145]
alpha-cleavage	M[analyte] − M[alkyl chain] (43, 71)	[52, p. 8]
benzylic bond cleavage	77, 91	[52, p. 16]
allylic bond cleavage	M[analyte] − M[alkyl chain] (41, 83)	[53, p. 22] [54, p. 230]
McLafferty rearrangement	51, 77, 105	[52, p. 102]
retro-Diels-Alder reaction	28, 54	[52, p. 138] [54, p. 70]
elimination of carbon monoxide	39, 51, 65, 66, 77, 78, 93	[54, p. 220]
loss of H_2O from alcohols	M[analyte] − 18, 31	[53, p. 40]
ortho elimination	M[analyte] − HZ*	[53, pp. 55–56]
heterocyclic compounds	40, 53, 66, 79 (varies)	[53, pp. 62–64] [54, pp. 94–95]

* Z refers to a hydrogen-accepting leaving group

An EI-Q-EM mass spectrometer depends on the separating instrument preceding it, to provide separation of different chemical compounds. Principle of operation of such MS instrument is that it scans over different masses over specified mass range within a specified period of time. This mass filtering is done by the quadrupole that works as a mass filter, also called: mass analyser. The width of the mass range affects the sensitivity and the time resolution of the produced analytical data. The smaller the range – the better the sensitivity and time separation, and vice versa. An extreme example of this phenomenon is the selective ion monitoring (SIM) mode of operation, in which the instrument only scans a few specified masses during the whole analysis period. In general, SIM mode offers superior sensitivity compared to the so called full scan mode. SIM method must be, however, always tuned for each sample component separately. This is because each chemical compound yields different fragment ions from EI ionisation.

Some instrument manufacturers offer MS instruments that can perform simultaneously SIM and scan measurements. This feature can take advantages from both methods. In pure SIM measurement a trade-off is made: characterisation capabilities of compounds is lost. This is due to the fact that the few number of ions that can be analysed in a SIM method, simply is not enough to determine a specific molecule. Full scan EI mass spectrum typically contains multiple peaks for each compound. However, the SIM method can be sometimes used to mitigate the effect of co-eluting interfering compounds. This is done by selecting ions into the SIM method that are specific to the desired analyte compound, but are not present in the interfering compounds. Overall, simultaneous SIM and scan operation of a mass spectrometer can be especially beneficial when working with unique samples. The heating step of the headspace sampling procedure may mean that samples containing heat-sensitive analytes can only be analysed once, as the delicate analytes might be exhaustively extracted or destroyed. Thus, separate SIM and scan analyses with such samples would not be possible.

2.3.1 Analysis of organic peroxides

One of the analytical challenges of organic peroxides is that their vapour pressures differ quite a lot from each other. TATP is very volatile at room temperature, whereas HMTD is barely volatile at all under the same conditions. This property makes the headspace sampling of these analytes much more complex. Another challenge is the different susceptibility to heat. HMTD decomposition reaction rate is about 260 times that of TATP at 151 °C [12], which can be seen as rather moderate thermal desorption temperature. To put this stark contrast into perspective, at 151 °C the half-life (or the time required for a half of an amount of substance to decompose) of HMTD is roughly 6.5 minutes whereas the half-life of TATP at the same temperature is about 28 hours.

For thermolabile analytes, the speed of analysis with a GC method can be seen as a vital factor. The less time the sensitive analytes spend under elevated temperatures, the less they undergo degradation due to the catalysing properties of heat. In a GC analysis, many parameters affect the elution time, or in other terms the time the analytes spend in the instrument. These parameters are for example: column length, stationary phase characteristics, carrier gas flow rate through the column, temperature program of the column and vapor pressure and other temperature characteristics of an analyte. However, many of these parameters come with trade-offs. Column length affects also the separation of compounds, if too short, closely eluting compounds might not be separated enough and co-elution occurs, possibly foiling the analysis. Longer column instead often offers a better separation and resolution, but analysis times are longer. Also, thin capillary columns can only carry limited gas flow through them, due to their narrow inner diameter. Typical convention of raising the column oven temperature to speed up analyte elution subjects analytes to higher thermal stress and might accelerate their decomposition during separation. For these reasons, optimal parameters must be found during method development phase by systematic trial and error experimentation.

2.3.2 Analysis of emulsion explosives

Analysis of emulsion explosives with a headspace GC/MS method can be assumed to be relatively straightforward. It has a well-established role in analysis of flammable substances, such as mineral oil based solvents [55, pp. 395–396]. However, it is also recognised that headspace sampling is not optimal for high boiling point petroleum products and especially not suitable for petroleum waxes. Headspace sampling temperatures are generally limited to roughly 100 °C for practical reasons. Also, typical headspace sample collector materials such as poly dimethyl siloxanes (PDMS) are susceptible to high temperatures in oxygen rich environments, such as air. The main interest of HS/GC/MS analysis of emulsion explosives is that how effectively the SHE sampling methods are capable of collecting the hydrocarbon components of emulsion explosives.

2.4 Capillary electrophoresis

Capillary electrophoresis (CE) is a separation method used in analytical chemistry. It is typically used for ionic samples, samples with an electrical charge, chiral molecules and proteomics. The separation is based on electrophoresis, or in other words, mobility of charged particles in solutions driven by voltage. However, distinct from other electrophoresis applications, CE separation is performed inside of a narrow bore capillary column that is filled with a conductive buffer solution. [56, pp. 867–869]

Capillary electrophoresis is typically used for separation of charged compounds or ions. Analytes get separated in CE because of three fundamental factors affecting the speed of movement of a particle inside the capillary: the charge of the particle, the diameter of the particle and the viscosity of the medium (i.e. the buffer solution). Another important aspect of capillary electrophoresis is the electro-osmotic flow (EOF). EOF is a phenomenon that arises from the fact that the silanol groups of the CE capillaries are negatively charged due to the presence of an electric field and an ionic solution. So-called double layer forms inside of the capillary, as counterions from the buffer solution are being attracted to the inner surface of the capillary tube. Thus, an immobile stagnant layer, sometimes called the Stern layer, is being formed. Inside of the capillary, a second layer forms, called the diffuse layer or the Gouy-Chapman layer. Cations in the diffuse layer are being pushed towards the cathode by an electric field, and as they move, they pull along the bulk of the solvent inside the capillary tube. A cross-sectional view of the CE capillary is shown in Figure 7. [57, pp. 2–4]

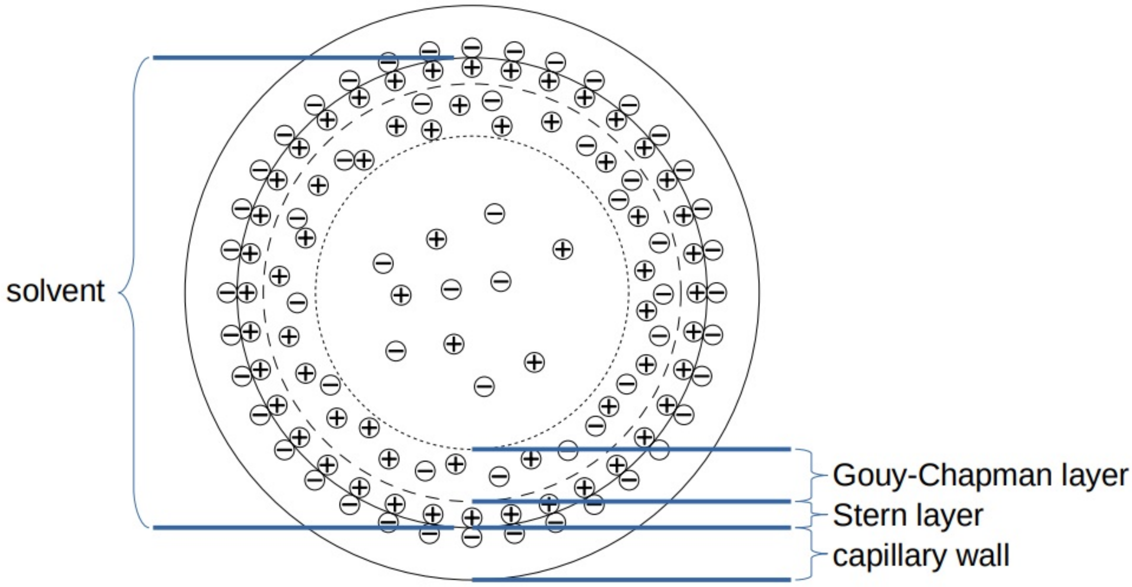


Figure 7: Cross-section of the CE capillary showing the double layer (picture not in scale) [57, p. 3]

Probably the most common type of detectors within CE instruments are optical detectors. These range from UV absorption detectors to fluorescence based ones. One very common and versatile variation is the UV-Vis diode array detector (DAD) that can operate at multiple different wavelengths. [57, p. 18] [56, p. 871] It must be noted, that in order for the absorbance based methods to work, the samples must have absorption in the ultraviolet range of electromagnetic radiation. In other words, they must have chromophores in their chemical structure. However, if the sample analytes do not have UV absorption, so-called indirect detection method can be used. This is done by doping the analytical buffer solution with chromophores that absorb UV light. When the sample analytes are moving in the capillary, they displace some of the chromophore particles, producing a lower absorbance signal as they are passing by the detector [58, p. 269] [56, p. 873].

Other types of possible detectors with CE instruments are, for example, mass spectrometers and nuclear magnetic resonance (NMR) instruments. Mass spectrometer can be seen as a very powerful and versatile detection method for a CE analysis. It offers a great sensitivity, structural information of the samples and has little limitations in regards of sample characteristics. [57, p. 19] These sophisticated detectors naturally come with their drawbacks too, namely complexity and high costs.

Analysis of neutral analytes with CE is possible with a special technique called micellar electrokinetic chromatography (MEKC). This technique is based on micelle formation tendency of surfactants and differential affinity of molecules to bind with the micelles. The most typical surfactant used for MEKC techniques is the sodium dodecyl sulphate (SDS) that has a strong negative net charge due to the sulphate functional group. The MEKC analyses are typically performed in strongly basic buffer solutions in order to promote a strong electro-osmotic flow. As a negative species, the SDS micelles resist the movement towards the cathode in the EOF. However, due to the strong electro-osmotic flow towards the cathode, the net flow of the micelles is also towards the cathode. Sample analytes that do not interact with the micelles will migrate to the detector with the EOF. Sample analytes that interact with the micelles completely, will be migrated later, due to the resistance of motility of the SDS, along with the micelles. [56, pp. 882–883], [59, pp. 65–67]

The surfactant molecules form an equilibrium between the micellar formation and free ion form. The equilibrium characteristics determine and enable the separation of different analytes with the MEKC technique. An important parameter of the MEKC technique is the critical micelle concentration (CMC). It means a threshold concentration of the surfactant in a buffer solution, below which the micelles are not forming. Thus, the surfactant concentration must be always higher than the CMC, in order for the method to work as intended. The CMC depends on the selected surfactant, the buffer solution, pH and possible solvents present in the buffer solution. [56, pp. 882–883], [59, pp. 65–67]

The analysis of organic peroxide explosives with a CE/DAD instrument is not quite straightforward. First obstacle is the solubility of peroxides. None of the three peroxides (TATP, HMTD or MEKP) is soluble in water. They are, however, soluble in solvents such as acetone and tetrahydrofuran (THF). The solubility issue might be avoided by dissolving the samples in an acetone-water mixture. This would also have to be the mode of operation if the method will be implemented for crime scene samples too. Debris samples would have to be extracted either with acetone-water mixture or pure acetone and then diluting the extract with water for CE analyses.

Another problem of organic peroxides from the viewpoint of CE analysis is their uncharged chemical structure. Uncharged particles have no motility in an electric field, for which reason they would elute at the EOF peak in the electropherogram. This could be fixed by using a MEKC method. However, it is unknown how the MEKC reagents, namely the surfactants, work or react with organic solvents present in the buffers.

Yet another problem with CE analysis of the peroxides is their inherent lack of UV absoption, as they have no chromophores in their chemical structure [8]. However, some sources have reported of TATP having UV absorption at around 240 nm [60], whereas others have reported successful absorption-based detection of TATP at wavelength of 200 nm [20]. The lack of UV absorption could be mitigated by doping the buffer solution with chromophores and using indirect detection. Such analytical MEKC buffer solution kits were not commercially available when the experiments of this work were carried out.

3 Research materials and methods

The aim of this work was to develop analytical methods for GC/MS and CE/DAD to facilitate the analysis of organic peroxide explosives and emulsion explosives. For both methods, the purpose was to determine the suitability of the technique for the intended purpose, optimise the method parameters and to determine the key values of analytical performance. These parameters were: limit of detection, repeatability, method ruggedness in the presence of matrices and sample recovery efficiency.

3.1 Materials

Of the peroxides, TATP and HMTD were synthesised in the laboratory from precursor chemicals, as no commercial certified reference materials were available. In turn, MEKP that was used in the experiments, was obtained from Sigma-Aldrich as a technical grade reference material (Sigma-Aldrich catalogue number 743003). Composition of the MEKP reference material is shown in Table 2. In addition, the MEKP product contained 2,2,4-trimethyl-1,3-pentanediol-diisobutyrate as a stabiliser. The amount of the stabiliser in the product was unknown. Precursor chemicals used for the TATP and HMTD syntheses were solvents of analytical grade acquired from Merck. Synthesis product qualities were confirmed with Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy to confirm that right products of the syntheses were obtained.

Table 2: Composition of the MEKP reference [36]

component	concentration
MEKP	50 – 70 %
4-hydroxy-4-methylpentan-2-one	30 – 50 %
ethyl methyl ketone	10 – 20 %

For emulsion explosive experiments, commercial products: Forcit Kemix and Forcit Kemix A were used. General composition of these products is shown in Table 3.

Table 3: Composition of the emulsion explosive samples [61]

component	concentration
ammonium nitrate	70 – 85 %
white mineral oil (petroleum)	5 – 6 %
aluminium powder (only Kemix A)	$\sim$ 5 %

3.2 Experimental

In this section, instrumentation and experimental procedures are being described. Experimental work done on the GC/MS was quite diverse, as the three organic peroxides were analysed as acetone dilutions and later extending the use of the method to headspace sampling. The GC/MS instrument was also used to study its capabilities for headspace analysis of emulsion explosives. Method development on the CE/DAD instrument was more straightforward, as the main interest was to test its performance in analysing organic peroxides in aqueous phase.

3.2.1 GC/MS

Instrument used for the GC/MS analyses was Agilent 7890 gas chromatograph coupled with Agilent 5975C single quadrupole mass spectrometer. Two different analytical columns were tested for the analyses – Agilent HP-5MS (30 m × 0.25 mm × 0.25 μm (film)) and Agilent DB-5 (15 m × 0.25 mm × 0.25 μm (film)). The GC/MS system was fitted with GL Systems Optic 4 multimode inlet. Optic 4 inlet has features that are typically not available in standard GC instrument inlets. These specialities include: pyrolysis capabilities, capability of performing large volume injections, thermal desorption, basic liquid injections and headspace sampling, all with the same inlet. Fritted liner (2414-1001) from GL Sciences was used for the thermodesorption and needle injection analyses. For SPME thermodesorption, empty liner with narrow inner diameter (2414-1005) from GL Sciences was used. Combined Wiley Registry 12th Edition/NIST 2020 mass spectral library was used for analysis and identification of mass spectra.

The Optic 4 system also has an on-column cryogenic trapping feature, whose effectiveness was tested to improve thermal desorption sample introduction. As the thermal desorption was performed for sorbent rods with relatively bulky sorptive matrix, the desorption process was significantly slower than from, for example, small-mass SPME fiber. The long desorption time may lead to widening of the analyte front as it is condensing at the beginning of the analytical column. The cryogenic trap focuses the analytes in an extremely sharp analyte front and rapid heating of the trap after the desorption ensures that the analyte front leaves the trap as a narrow band. For the cryotrap, liquid carbon dioxide (CO_2) was used as a cooling medium.

Headspace sampling tests were performed with Gerstel Standard PDMS-Twister SBSE rods. Two sizes of Twister rods were tested: 10 mm and 20 mm in length, both with 0.5 mm film thickness. For HMTD, SPME fiber headspace extraction was tested with Supelco 100 μm PDMS SPME assembly (cat. no 57300) with Supelco manual SPME holder (cat. no 57330-U).

Initial GC/MS parameters were based on an existing analytical method in the laboratory. These parameters are shown in Table 4. At first, suitability of the GC/MS analysis for the peroxides was tested for acetone dilutions of the peroxides. This procedure ensures that precise amount of sample is being introduced into the instrument, without uncertainties of sample recovery efficiency. Liquid injections were performed with Agilent manual 10 μl GC syringe (part number 5190-1483).

Table 4: Initial parameters of the GC/MS method

parameter	value
inlet temperature	210 °C
injection type	splitless
column flow	1 ml/min
analytical column	HP-5MS *
column length	30 m
column inner diameter	250 μm
column phase thickness	0.25 μm
inlet temperature	210 °C
column oven initial temperature	40 °C (1 min hold)
column oven heating ramp	15 °C/min
column oven final temperature	240 °C
mass spectrometer transfer line temperature	325 °C
ion source temperature	230 °C
quadrupole temperature	150 °C
scan region	40–550 m/z

* (5 % phenyl)-methylpolysiloxane

Main concern related to the GC/MS analysis of the peroxides was their thermal lability. This feature was the primary guiding factor of the method development. Figure 8 illustrates the vast number of parameters related to headspace analysis. All of the parameters shown in Figure 8 were tested and optimised. Tests were carried out over a broad region with evenly spaced values. Then, for each parameter, values that produced the best signal feedback were chosen for the final method.

Method development was started with TATP with liquid injections. An acetone dilution of the TATP synthesised in the laboratory was made by weighing 5 mg of it into a 10 ml volumetric flask. This solution was then further diluted with acetone to 1:10 and 1:100 dilutions. Optimal parameters of the GC/MS instrument were then iterated using the 1:100 dilution of the TATP.

After finding the optimal parameters for the liquid injection analysis of TATP, the development of the headspace method was started. At first, the effectiveness and suitability of the thermodesorption of the SBSE rod was tested. This was done by spiking the 1:100 acetone dilution of TATP directly on the SBSE Twister rod. After letting the acetone to vaporise from the rod for a few seconds at room temperature, the rod was placed into a fritted liner in the Optic 4 inlet. After this, thermodesorption method on the instrument was started. Parameters regarding the thermodesorption were then optimised by performing the SBSE spiking thermodesorption analyses.

Finally, headspace sample recovery parameters were optimised, such as headspace sample collection time, collection temperature, container volume and SBSE sorbent rod dimensions. Headspace collection experiments were carried out by spiking the 1:100 acetone dilution into an Erlenmeyer flask and closing the flask tightly with a

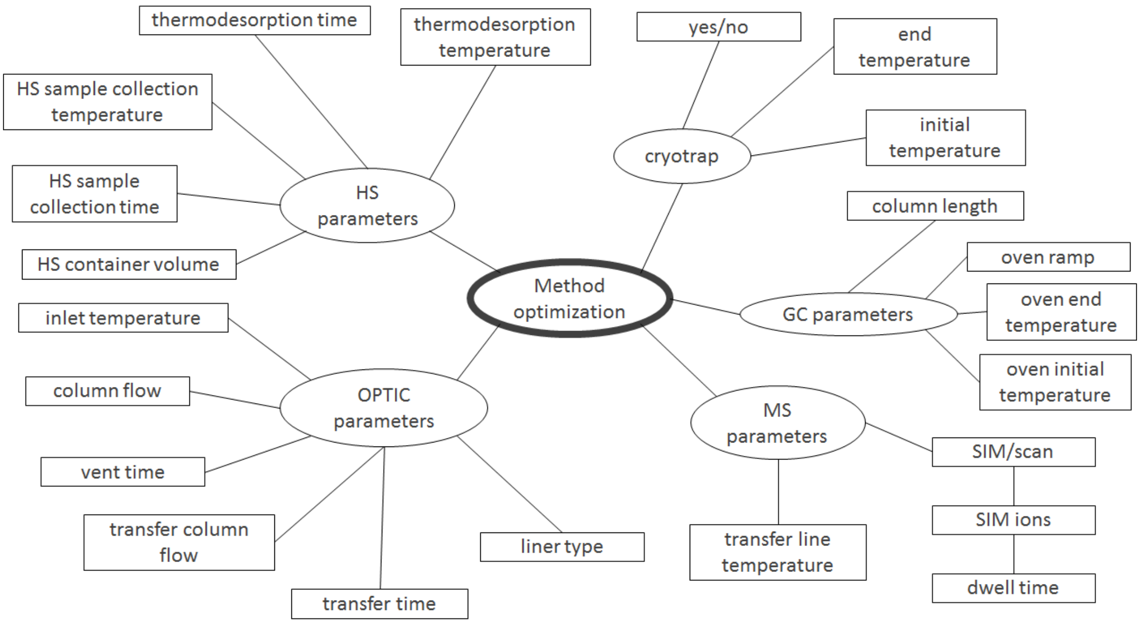


Figure 8: Different parameters affecting the headspace analysis with the Optic 4 GC/MS system

ground glass stopper. A Twister SBSE sorbent rod was placed inside the flask and was held in place on the side of the flask by attaching a magnet on the outside of the flask with tape. This test setup is illustrated in Figure 9. The flask was then heated for a certain period of time in an oven at elevated temperature. Finally, the SBSE sorbent rod was taken out of the headspace container and placed into the inlet of the GC/MS instrument for thermodesorption. The headspace mode of operation corresponds to the actual sampling process in the final method for trace samples, as debris from the crime scene can be inserted into the flask and heated in an oven in order to collect a headspace sample. Different sizes of Erlenmeyer flasks were tested as headspace containers, in order to determine the effect of the headspace volume to the sensitivity of the method. Flask sizes of 50, 100 and 250 ml were tested.

After encountered difficulties with thermodesorption of HMTD from the SBSE rod, traditional gas phase SPME technique was experimented. At first, feasibility of the thermodesorption was experimented for HMTD by spiking acetone dilution of HMTD directly onto the SPME fiber. After a few seconds as the acetone evaporated from the fiber, the SPME device was placed into the inlet of the GC/MS instrument and thermodesorption was started. Actual headspace sampling was tested mainly in the same way as for TATP with SBSE sorbent rod system – except, acetone dilution of the HMTD was spiked into a 40 ml headspace vial that was then closed with a stopper equipped with a PTFE septum. The SPME device needle was then pressed through the septum and after exposing the fiber, the system was heated in an oven for a given period of time. Finally after the heating, the SPME device was then placed into the inlet of the GC/MS instrument and thermodesorption was started. The headspace procedure with the SPME apparatus is illustrated in Figure 9.

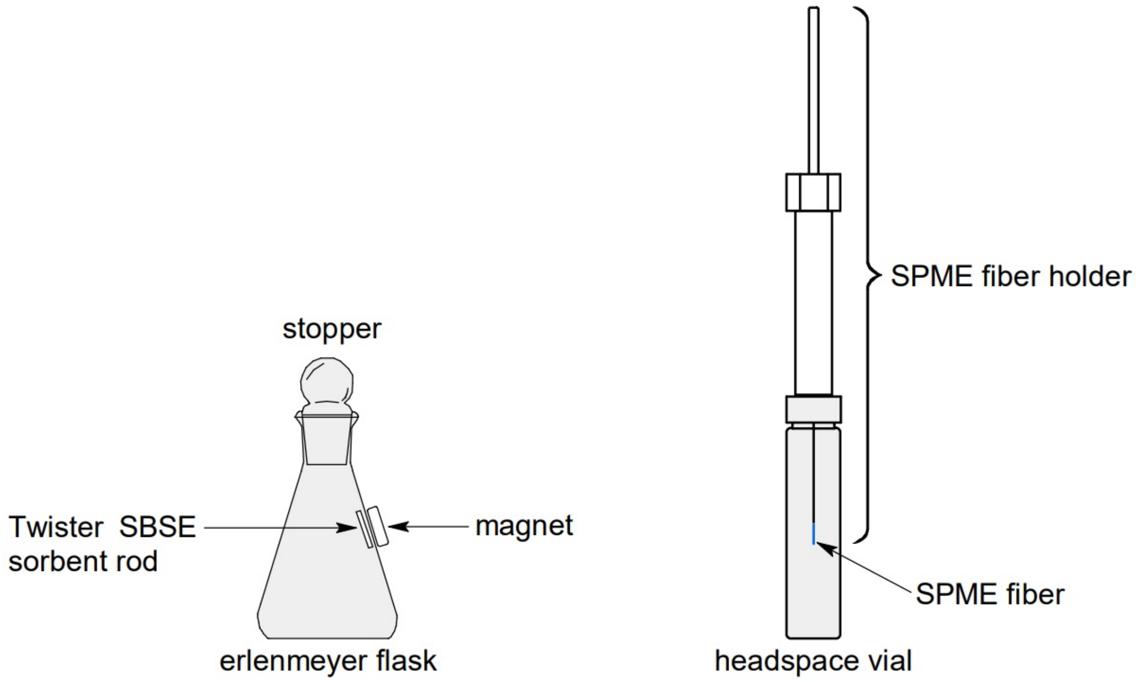


Figure 9: Test setups for headspace sample recovery optimisation; *on the left:* setup for the SBSE sample recovery for TATP; *on the right:* setup for the SPME sample recovery for HMTD

Explosion residue analyses of TATP were conducted by weighing 50 mg of solid TATP onto a 15 × 15 cm piece of aluminium foil and wrapping the foil loosely into a package. Then the package was placed onto an anvil inside of a blasting chamber and the package was hit with a hammer. Subsequent explosion was apparent due to the loud noise of the explosion and shredding of the aluminium foil. Quickly after the explosion, pieces of the foil were collected and placed into a 100 ml Erlenmeyer flask which was closed with a ground glass stopper. During the same day, HS/GC/MS analysis of the foil pieces was carried out with the SBSE headspace technique. After the HS analysis, the stopper was removed and the flask was left to sit open at room temperature over night. The same sample was then analysed again with the SBSE HS technique to determine how much of the TATP traces were lost during 24 hours at room temperature.

Different matrices were analysed with the SBSE headspace technique to determine if common sample matrix materials cause interference to the analyses. For this purpose polyethylene (PE) plastic, paper and aluminium foil were tested. These tests were carried out by cutting a 10 × 10 cm size piece of each material and placing them into 50 ml Erlenmeyer flasks. Then the HS analysis process was conducted on them.

Analyses of MEKP on the GC/MS were conducted by diluting the commercial MEKP product in acetone in 5 μl/10 ml ratio. Further dilutions in 1:10 and 1:100 ratios were also prepared of the stock solution in acetone. Liquid injections for MEKP were analysed in the same manner as for TATP and HMTD as described previously. Headspace sampling was not tested for MEKP, for reasons described in the next section.

Headspace sampling and analysis for emulsion explosives was done essentially in the same manner as for TATP. Approximately 5 g of the solid packaged emulsion explosive was broken off and placed into a 50 ml Erlenmeyer flask and heated in an oven with an SBSE sorbent rod sample collector. After the headspace sampling, thermodesorption of the sorbent rod was carried out similarly as described above.

3.2.2 CE/DAD

Capillary electrophoresis method development was performed on Sciex P/ACE MDQ Plus instrument. A CM Scientific Polymicro Technologies flexible fused silica capillary with 75 µm inner diameter and 50 cm effective length (length from the inlet end of the capillary to the optical window) was used for all CE experiments. Other instrument parameters used for the analyses, are shown in Table 5. Analytical buffer solution kit CEofix MEKC from Analis was used for all analyses. The kit consists of: borate/polycation buffer (pH = 9.1) initiator solution, borate/SDS buffer (pH = 9.2) accelerator solution and a borate/SDS buffer (pH = 9.1) diluent solution. Also, a special test mix containing analytes: dimethylformamide, phenylacetic acid, tryptamine and sulconazol, was included in the kit.

Table 5: Instrument parameters of the CE/DAD method

parameter	value
detection wavelength	190 nm
cartridge temperature	20 °C
separation voltage	25/30 kV
separation duration	15 min
injection method	pressure
injection pressure	0.1 psi
injection duration	10 s
polarity	normal

Samples for the CE analyses were prepared by dissolving a few milligrams of the peroxides into an acetone-water mixture. Different ratios of acetone and water were tested along with testing different separation voltages on the instrument. Also, to ensure the formation and stability of the analyte containing micelles in the sample solutions, another dilutions were made by diluting the peroxide-acetone solutions with the MEKC buffer.

4 Results and discussion

All experiment results are presented and discussed in this chapter. Results of the gas chromatography method development and capillary electrophoresis are divided into following subsections: 4.1 GC/MS method development and 4.2 CE/DAD method development.

4.1 GC/MS method development

Experiments gave varying results of the GC/MS analysis for the three organic peroxides. Suitability of the analytical technique was different for each of them, especially in terms of the headspace sample collection. The analytical results of the emulsion explosives were moderate for the GC/MS part. Headspace sampling of them, in turn, proved to be sub-optimal.

4.1.1 TATP

Experiments for TATP analysis with GC/MS were started with a basic method used in the laboratory. The parameters of this method are shown in Table 4. A solution of TATP was prepared by weighing 5 mg of solid powdery TATP into a 10 ml volumetric flask that was then filled with acetone. Further dilution 1:100 in acetone was then prepared from it. Thus achieved 5 μg/ml solution was then used throughout the experiments.

Initial method provided relatively good results for TATP as acetone solution liquid injection. TATP was easily recognised from the chromatogram by its mass spectrum and it was identified by the mass spectrum library with a satisfactory match score. However, observed peak shape was not optimal, as can be seen in Figure 10. The main problem was moderate peak tailing and uneven shape of the peak. Peak tailing makes the peak wider and sets difficulties to determine the ending point. Widening inevitably decreases the peak height, thus leading to a poorer signal-to-noise ratio. In order to optimise a trace analysis method, signal-to-noise ratio should be maximised in order to obtain the best possible limit of detection.

The effect of column length on analysis of TATP was determined with liquid injection of an acetone dilution of the peroxide. Both tested columns gave sufficiently good results for TATP. For the 30 m HP-5MS column, certain amount of inevitable peak tailing was observed for the TATP peak. In turn, the shorter DB-5 (15 m) column produced a sharper peak, but peculiar peak tailing for it was observed. Corresponding chromatograms are shown in Figure 11.

The effect of inlet temperature on analysis of TATP was tested with liquid injections at four different temperatures (70, 150, 210 and 250 °C). It was noted, that at higher temperatures the signal feedback started getting worse. It is likely that high temperature reduces analyte recovery as thermal degradation begins to increase. The lowest inlet temperature tested (70 °C) yielded the highest signal feedback. Corresponding chromatograms are shown in Figure 12.

Retention time repeatability of TATP was determined with liquid injections. The purpose was to prove, that the instrument can perform such analysis for the peroxide

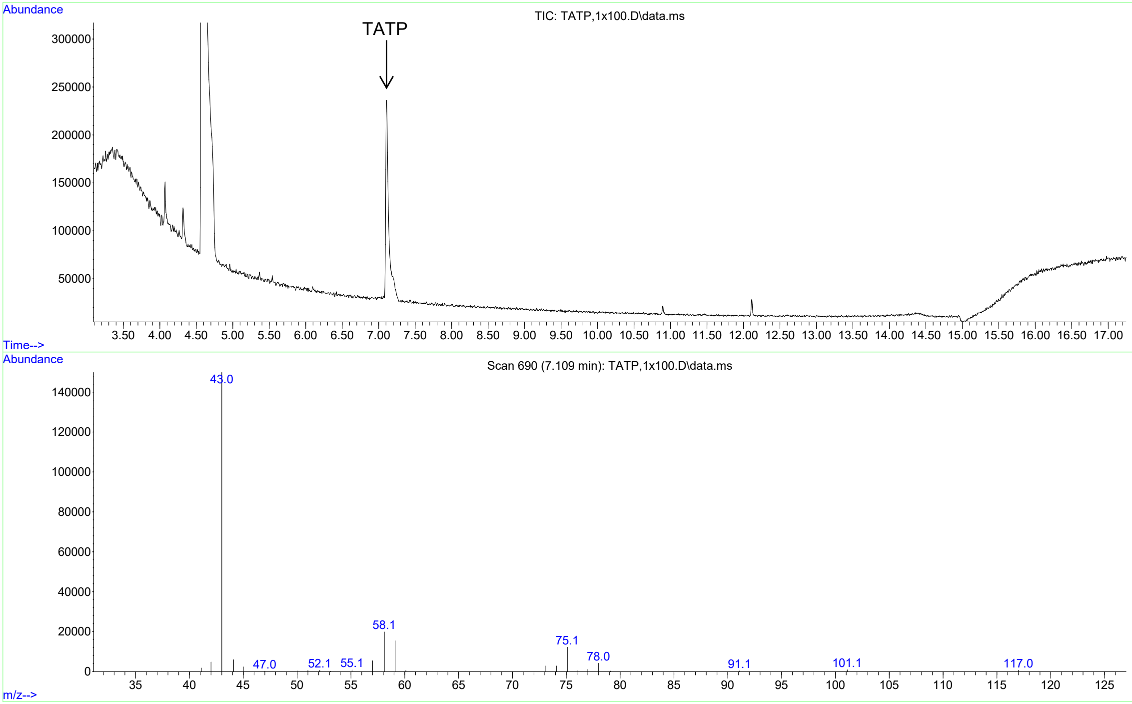


Figure 10: Initial analysis result of TATP liquid injection, 1 µl of 5 µg/ml solution injected, *above*: chromatogram of the analysis, *below*: mass spectrum of the TATP peak

with good repeatability. Repeatability of TATP retention time was extremely good. Of six repetitions, standard deviation of 0.00649 minutes was observed. Generally in chromatography, retention time window of ±0.05 minutes is considered acceptable. The obtained result fulfils this requirement with satisfactory margin. Corresponding analytical results are shown in Table A1.

Impact of the mass spectrometer transfer line temperature on the recovery of the TATP in GC/MS analysis was tested at two different temperatures. Tested temperatures were 325 °C and 230 °C. Between these temperatures, there were no difference either in sample recovery efficiency or mass spectrum quality. Results at both temperatures were practically identical.

The effect and feasibility of the cryotrap system for TATP was initially tested with liquid injections. Results show that cryogenic trapping is compatible with TATP without significant interference, and that it enhanced the peak height but did not affect the peak area. The effect of peak sharpening is favorable, as it yields a better signal-to-noise ratio for the method, and thus enables lower LODs to be achieved. Corresponding analytical results are shown in Table A2.

Thermodesorption feasibility of the SBSE sorbent rod for TATP analysis was studied by spiking acetone dilution of TATP onto a Twister rod. Optimal thermodesorption temperature was determined to be 210 °C. Low thermodesorption temperatures showed weaker signal feedback for TATP, presumably due to the analyte

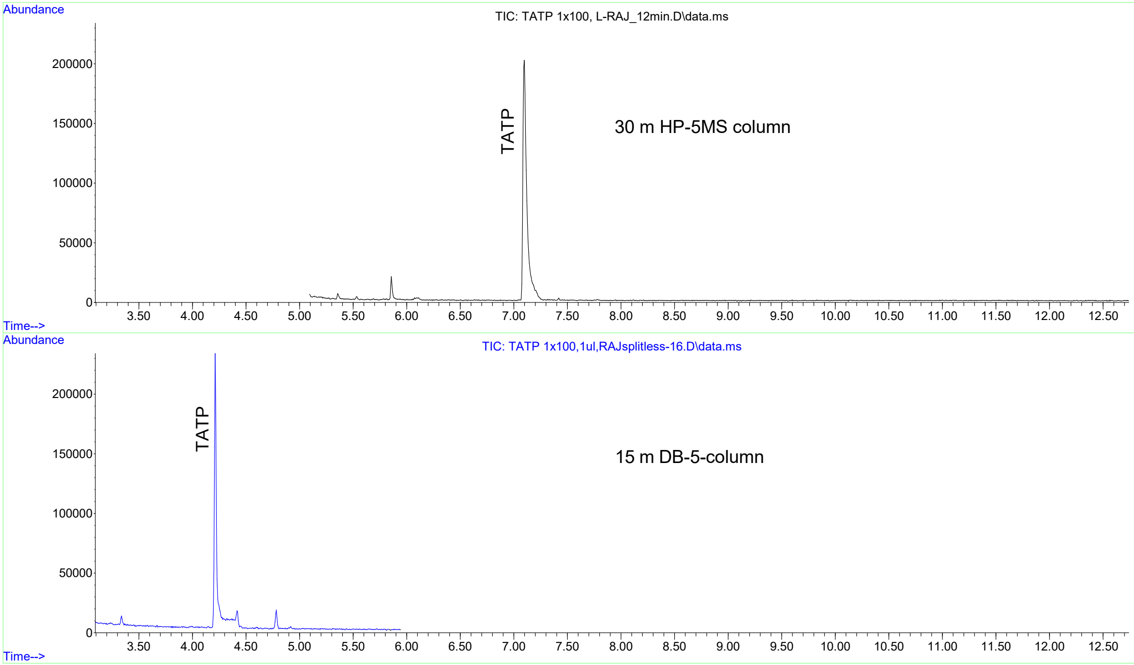


Figure 11: The effect of column length in TATP liquid injection analysis, 1 µl of 5 µg/ml solution injected

not evaporating quickly enough. For 70 °C no peak at all was detected. Higher thermodesorption temperatures showed stronger signal feedback but simultaneously, interfering matrix peaks became more abundant. After determining the mass spectra of the matrix peaks, it was deducted that the interfering peaks originated from the Twister sorbent material. Peaks were recognised as polysiloxanes, which is the sorbent material of the Twister SBSE rods. Corresponding analytical results are shown in Table A3 and Figure 13.

After determining that thermodesorption of TATP with the SBSE sample introduction is possible without major losses of the analyte, optimal thermodesorption time at 210 °C was to be determined. Thermodesorption times of 3 and 5 minutes were compared. Results show that increasing the time to 5 minutes does not increase sample recovery efficiency or offer other benefits. Shorter time of 3 minutes is seen as more beneficial in terms of shorter total duration of the analysis. Table A4 shows corresponding analysis results.

The effect of carrier gas flow inside the inlet during the thermodesorption phase of the SBSE sample introduction was studied. The thermodesorption was naturally performed in spitless configuration to avoid any loss of the sample into the split line exhaust. The sorbent matrix is flushed with the chromatography carrier gas for the whole duration of the analysis. Firstly, the carrier gas flow transfers the evaporated analytes from the inlet to the column of the instrument, and secondly, the gas flow protects the sorbent material from oxygen during the high temperature thermodesorption phase. Gas flow rates of 1, 2 and 4 ml were tested. Flow rate of

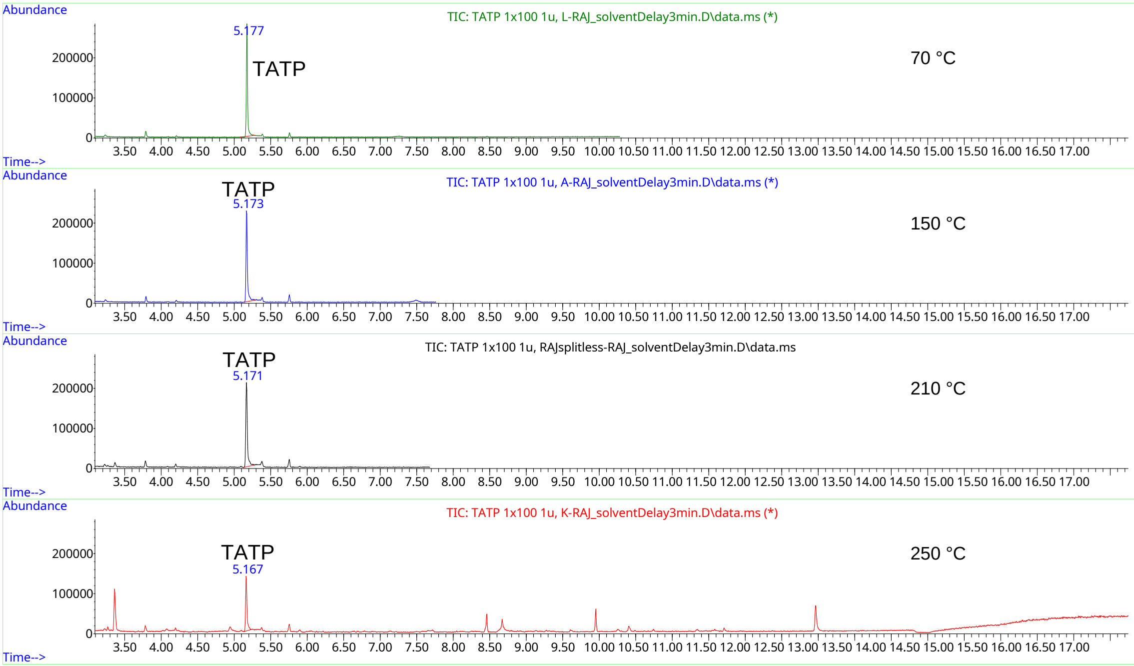


Figure 12: The effect of inlet temperature on TATP liquid injection, 1 µl of 5 µg/ml solution injected, TATP showing a sharp peak around 5.17 minutes in each chromatogram, DB-5 (15 m) analytical column used for each run

4 ml showed the best sample recovery efficiency, but flow rate of 2 ml showed the best balance. Lower flow rate yielded satisfactory results and saves expensive helium gas. Table A5 shows corresponding analysis results.

After the parameters of the thermodesorption sample introduction were optimised, its sample recovery efficiency was compared to the acetone dilution liquid injection results of TATP. The same dilution that was analysed as a liquid injection, was spiked in same quantity onto an SBSE collector rod and thermodesorption sampling was performed. The results show excellent sample recovery efficiency with thermodesorption, well over 90 % of the liquid injection sample introduction. Results are shown in Table A6.

The effect of cryogenic trapping for thermodesorption was experimented. It was observed, that trapping enhances the peak shape significantly but the final temperature of the trap was determined to be indifferent between 100 °C and 210 °C. Results are shown in Table A7 and Figure 14.

With the good results of the SBSE technique thermodesorption, actual headspace sample collection capabilities of the sorbent rod was tested. These properties were tried at different headspace container volumes. Simultaneously, the effect of the size of the SBSE sorbent collectors was tested. Different headspace heating temperatures and times were experimented. Conclusively, the 20 mm Twister SBSE collector showed better performance than the 10 mm counterpart. The shorter rod produced weaker signal feedback in larger headspace container, which is significant as the size

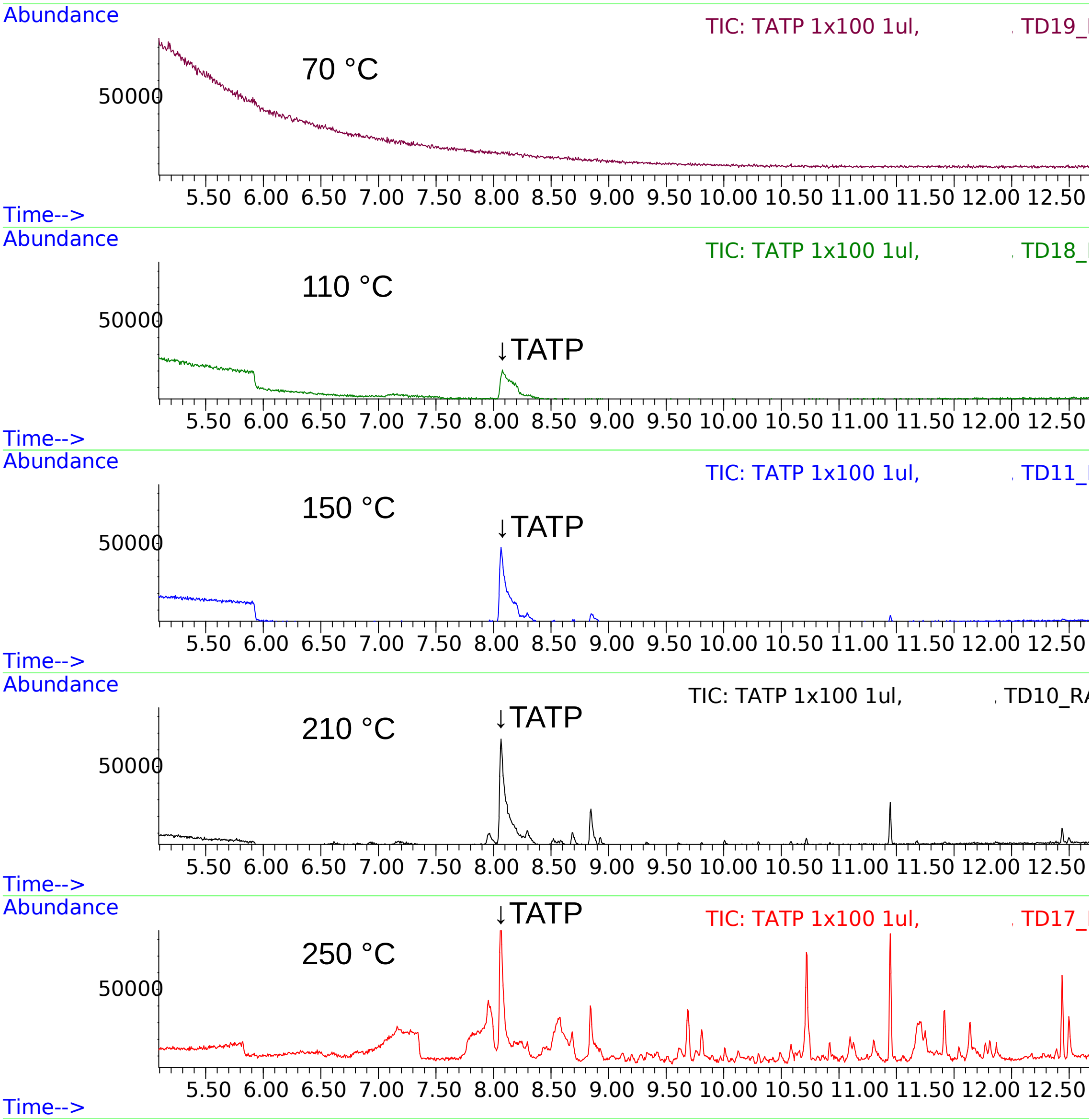


Figure 13: Effect of the thermodesorption temperature of TATP from Twister sorbent rod, TATP as acetone dilution spiked onto 10 mm Twister, TD temperature of 250 °C exhibits the best sample recovery efficiency, but also the most interference from thermal degradation of the sorbent material

of the headspace containers might vary in the actual applications of the method. For a moderate size headspace container, 30 minute sample collection time proved to be nearly as good as 60 minute collection time. Sample collection at 40, 50 and 60 °C yielded nearly identical results. Results are collectively shown in Table 6.

With the optimised parameters of the headspace collection, a comparison was made to determine the sample recovery efficiency. Headspace sample collection and subsequent thermodesorption sample introduction proved to be capable of averaged

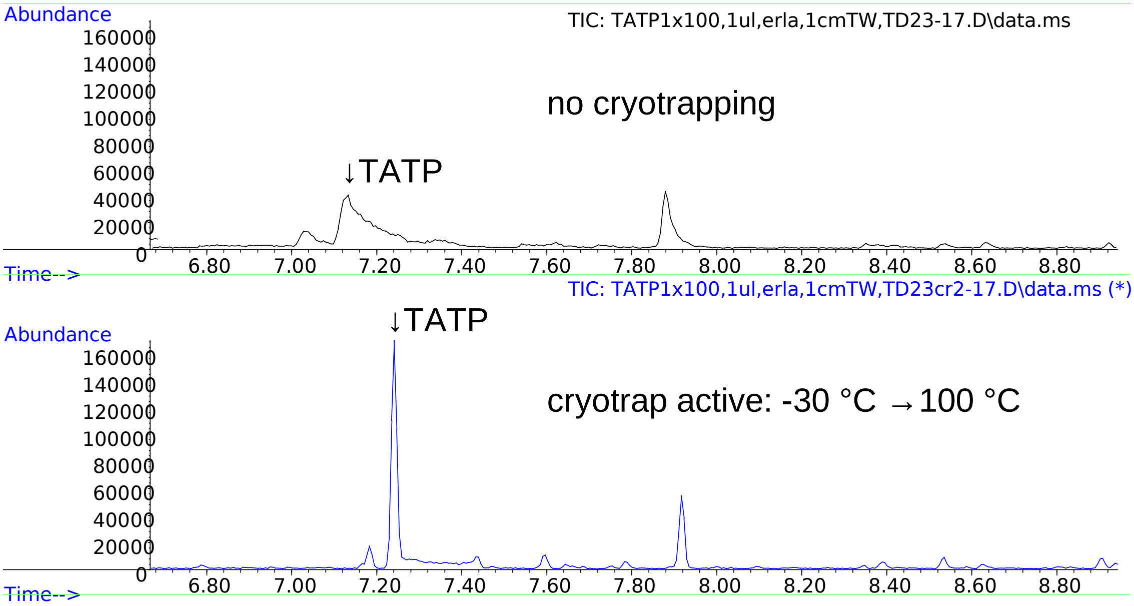


Figure 14: The effect of cryotrapping on thermodesorption of TATP, trapping significantly improves the sharpness of the peak

Table 6: Summary of results of the headspace sampling parameters, altered values are highlighted with boldface in the table

V_{inj} µl	$l_{Twister}$ mm	V_{HS} ml	T_{HS} °C	t_{HS} min	I_{peak}	I_{peak}/I_{max} %	A_{peak}
1	**10**	50	60	30	161400	100	1572800
1	**20**	50	60	30	132900	82	1320100
1	**10**	**50**	60	30	161400	100	1572800
1	**10**	**100**	60	30	113770	70	1116000
1	**20**	**50**	60	30	132900	92	1320100
1	**20**	**100**	60	30	144450	100	1380750
1	**20**	**250**	60	30	141700	98	1347400
1	20	250	60	**30**	141700	87	1347400
1	20	250	60	**60**	162000	100	1489000
2	20	50	**40**	30	297700	100	-
2	20	50	**50**	30	293800	99	-
2	20	50	**60**	30	257000	86	-

48.9 % sample recovery efficiency. The test was conduced by injecting 1 µl of the 5 µg/ml TATP solution into a 50 ml Erlenmeyer flask. Headspace sampling was then carried out with a 20 mm Twister sorbent rod at 60 °C headspace temperature for 30 minutes.

Ruggedness of the optimised method was tested in the presence of matrices. Aluminium foil did not produce any peaks to the chromatogram, thus non-volatile matrices supposedly do not interfere with the headspace method. Paper from a newspaper and polyethylene plastic film were analysed with the headspace method and both produced interfering peaks due to release of volatile compounds. Both matrices showed extremely intense peaks at TATP retention time and would thus deny the possibility to detect TATP traces in such matrices. Analysing the mass spectra of the interfering peaks, strong intensity mass fragments were found at m/z 43 and 57, both of which are important mass fragments of TATP as can be seen in Figure 10. Mass fragment of m/z 58 is one of the key fragments of TATP, and also one of the most intense ones. However, it cannot be used as a part of the SIM method because of the abundancy of mass fragment m/z 57 in many compounds. The fragment m/z 57 originates from a common butyl carbon chain and fragment m/z 58 is one of its isotope peak fragments.

A simultaneous SIM and scan mass detection method was implemented because of the matrix effects. Following ions were chosen for the SIM detection: m/z 75, 101, 117 and 222. Scan range was kept the same: m/z 40 – 550. The SIM/scan method proved to be very effective in combating the sample matrix interferences and the sensitivity of the scan detection was not noticeably injured. Figure 15 shows successful mitigation of matrix interference of a polyethylene plastic film with SIM/scan technique. With scan detection, the signal of the TATP reference was completely indistinguishable from the strong interference. With SIM detection the interference was completely gone. These results were achieved by comparing three different analytical runs. One sample was only the TATP being spiked into a headspace flask. This sample was used as a reference to determine the TATP intensity level. One sample was only the plastic material in a headspace flask. This sample was used to define the interfering matrix compound profile. The third sample was piece of the plastic material spiked with the TATP solution. This sample was used to study whether the TATP peak can be detected from the matrix. Used TATP reference was 1 µl of 5 µg/ml TATP acetone solution in a 50 ml Erlenmeyer flask. Analyses with the SIM/scan method showed similar results with paper sample matrix, removing essentially all interferences. Lowering of the headspace sampling temperature from 60 °C to 40 °C was observed to reduce the matrix effects, but in practice the effect was meaningless, as the intensity of the interfering peaks was still exceedingly high.

The limit of detection of the SBSE headspace GC/MS method was determined by making further dilutions of the TATP acetone solution. An acetone dilution of TATP in 0.5 µg/ml concentration was prepared and analysed with the parameters given in Table 7. Achieved signal feedback level of this analysis was determined to be the LOD of the method. Obtained result yields value of 500 pg of TATP in 50 ml headspace volume for the LOD. Determination of LOD for qualitative headspace methods can

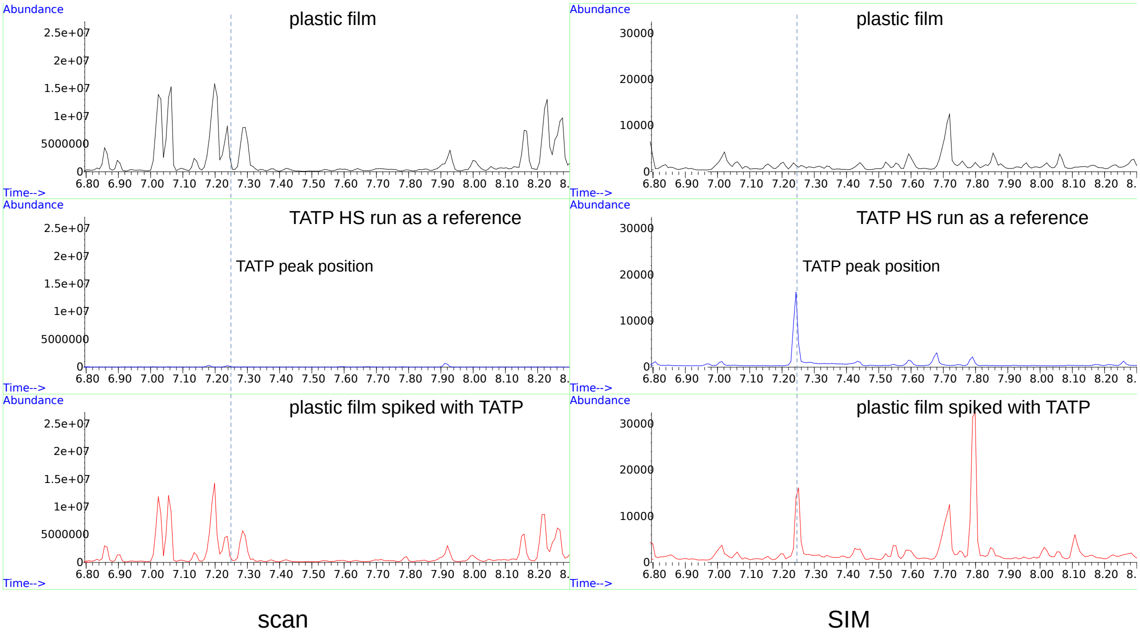


Figure 15: Successful mitigation of matrix interferences of plastic sample matrix; on the left: scan chromatograms of a plastic film, TATP HS analysis and a plastic film spiked with TATP solution; on the right: SIM chromatograms of a plastic film, TATP HS analysis and a plastic film spiked with TATP solution, *note:* the SIM and scan chromatograms are at separate scales

often be a challenge. Many parameters affect the final level of the signal feedback of the sample. These parameters include, for example, the volume of the headspace container, which will vary for this method in real applications because sample object sizes can vary significantly. Also, other volatile compounds possibly present in the sample affect the headspace equilibrium and thus the recovery of a specific compound. The determined LOD can be seen as a guiding value describing the method in a best-case-scenario without the presence of interfering matrices. Chromatograms of the LOD determination are shown in Figure 16.

Table 7: Analysis parameters used for the determination of the LOD

parameter	value
V_{HS}	50 ml
V_{inj}	1 µl
l_{Twister}	20 mm
T_{HS}	60 °C
t_{HS}	30 min

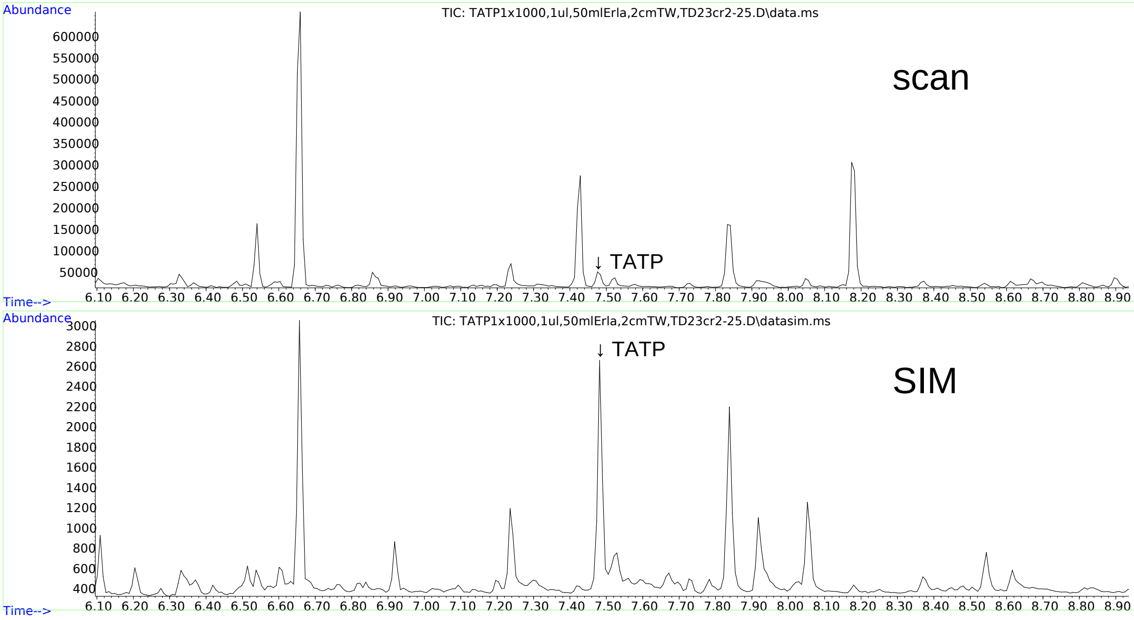


Figure 16: Scan and SIM chromatograms of determination of LOD for TATP

Finally, the method's capabilities were tested on an actual TATP explosion residue sample. A sample of TATP wrapped in aluminium foil was set off by hitting it with a hammer. After the explosion, pieces of the foil were collected and placed into an Erlenmeyer flask. The analysis yielded surprisingly strong signal, even overloading the instrument, which was observed by extremely broad peak in the chromatogram. Such overloading, however, is not a problem from the viewpoint of a qualitative trace analysis method as long as the mass spectrum of the analyte is not lost or distorted. Another experiment was carried out after the residue sample was analysed. After the HS analysis, the stopper was removed and the flask was left to sit open at room temperature over night. The same sample was then analysed again with the SBSE HS technique to determine how quickly such residues might evacuate from a sample. The results show, that nearly all residues were lost in 24 hours. Corresponding chromatograms are shown in Figure 17.

The experiment described above demonstrates the adverse effects of TATP volatility. It was observed that TATP traces were lost nearly completely in under 24 hours, when the sample was stored in well-ventilated environment. This should be taken into consideration when working with possible TATP-related incidents; samples must be collected from the incident scene as soon as possible after the event. Also, it is vital that the samples are stored in gas-tight containers, preferably with as little airspace as possible. In optimal working procedure, the sample container could be also used as the headspace container. Such arrangement would minimise the risk of losing the possible evaporated TATP traces. Using gas-tight fire debris bags for the sample storage and headspace sampling could be one possibility. However, their

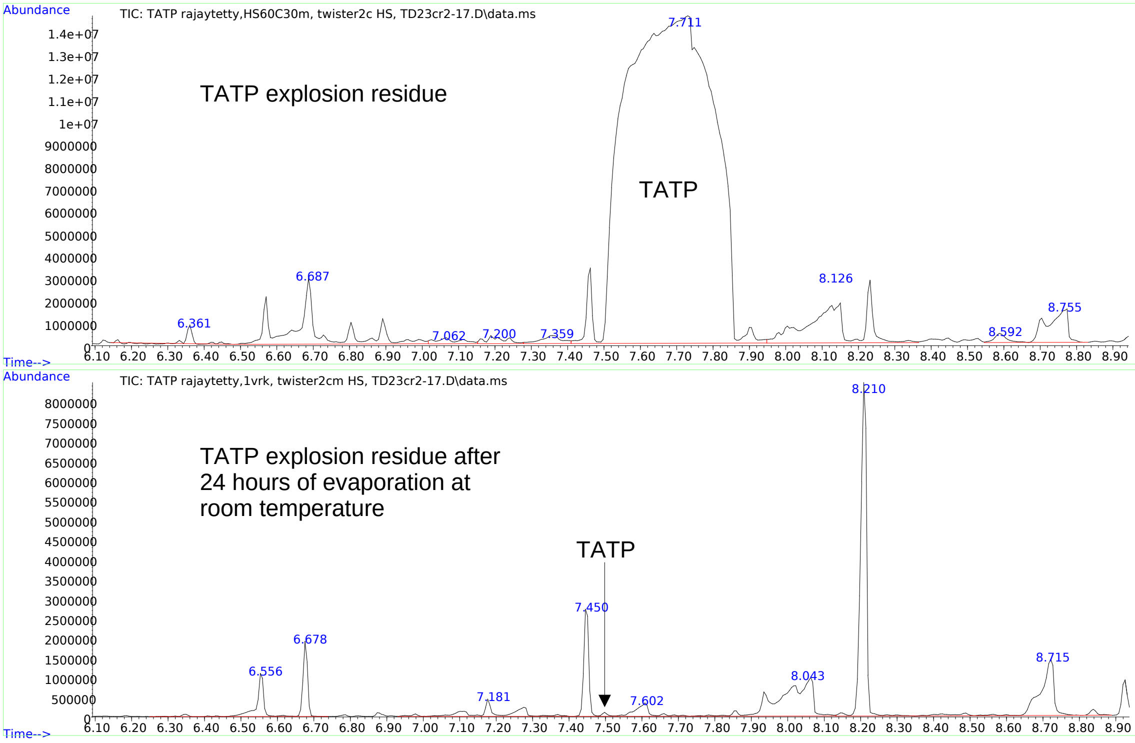


Figure 17: Headspace analysis of TATP residue after explosion from aluminium foil; above: headspace analysis of TATP explosion residue of a sample collected soon after the detonation; below: headspace analysis of the same sample after overnight exposure to open air

suitability and performance must be validated for intended use, if desired to be implement to the procedure.

An identified weakness of the trace analysis headspace method is its susceptibility to sample matrix effects. The SIM/scan mode of operation of the GC/MS can negate some of these interferences, but it also has its weaknesses. The downside of the SIM mode is that it does not have the same characterisation capabilities as the scan mode, which is a problem in cases where there are a lot of interfering compounds in the scan data. A special practice was observed to be useful during the method development phase: there were cases where sample matrix compounds were rendering the scan data useless, but not showing interference in the SIM data. In such cases, suspected TATP samples can be analysed by first following the normal HS sampling procedure with the SBSE, then exposing the sample to open air for a given period of time and then analysing the sample again with HS/GC/MS method. Given the quick loss of TATP traces, changes in the SIM data can be observed to determine whether there were TATP traces in the sample in the first HS analysis. This is possible because the volatile matrix compounds typically do not evaporate as quickly and exhaustively. The described procedure is quite unconventional, but might be one of the few possible ways to make the most of the non-characteristic SIM data. Most recommended sample matrix materials are those with least volatile interference compounds, such as glass, metal and stone. It would be highly recommended that pure sample matrices would always be sent along with trace samples from a crime scene. These blank sample matrices could be used as a reference to determine the vapour profile of each matrix material.

During the method development phase, it was noticed that the SBSE sorbent rods give off interfering compounds during thermodesorption after being stored at room temperature being exposed to air. The developed method and analytical technique are such sensitive, that even very small amounts of volatile compounds are visible in the analytical results. Thus, a recommended mode of operation is to always perform one blank thermodesorption run for the SBSE sorbent rod before using that specific rod for the headspace sampling. By doing so, majority of the interfering peaks from the sorbent material can be avoided.

4.1.2 HMTD

Acetone solutions for HMTD were prepared in the same way as described above for TATP. Method development for GC/MS analysis of HMTD was started with liquid injections of HMTD. Experiments were started using the 30 m HP-5MS analytical column. Temperatures of the GC/MS instrument were significantly lowered to better facilitate the analysis of the thermolabile HMTD. The MS transfer line temperature was set to 170 °C.

Initial tests on HMTD with the existing GC/MS method yielded poor results. No proper peak for the HMTD was to be observed. A broad, bell-shape curve rising from the baseline was present instead. It was identified as the HMTD by its mass spectrum. Fragment ions m/z 43 and 73 were especially prevalent, giving hint of degradation of HMTD. The mass spectrum combined with the broad and low abundance peak, strongly suggested thermal degradation of the analyte during chromatographic separation. If the HMTD would had disintegrated already before the injection, or immediately after it, most probably no peaks would have been detected, considering the low mass decomposition products of HMTD. However, as this was not the case, it is presumable that the analyte slowly decomposed in the column during the separation phase.

In effort to speed up the elution of HMTD, carrier gas flow in the column was raised from 1 ml/min to 2 ml/min. This change resulted in significant enhancement of the peak shape. Yet, a considerable amount of peak broadening could still be observed. Corresponding chromatograms are shown in Figure 18.

Next, optimal inlet temperature for the analysis was iterated. Three different temperatures were tried: 100, 150 and 200 °C. Of these three, 150 °C gave the best results. Corresponding chromatograms are shown in Figure 19.

Impact of the initial column temperature was studied. Five different initial temperatures were tried, keeping other parameters constant, including the column oven heating ramp rate of 16 °C/min. Tested temperature were: 50, 80, 100, 110 and 140 °C. Surprisingly, the lowest initial temperature did not yield the best results. Instead, middle temperatures 100 and 110 °C gave the best peak shape and height. Presumably this is due to the shorter analysis time, albeit at a higher temperature. Thus HMTD is exposed to high temperatures for a shorter period of time. Corresponding results are shown in Figure 20 and Table 8.

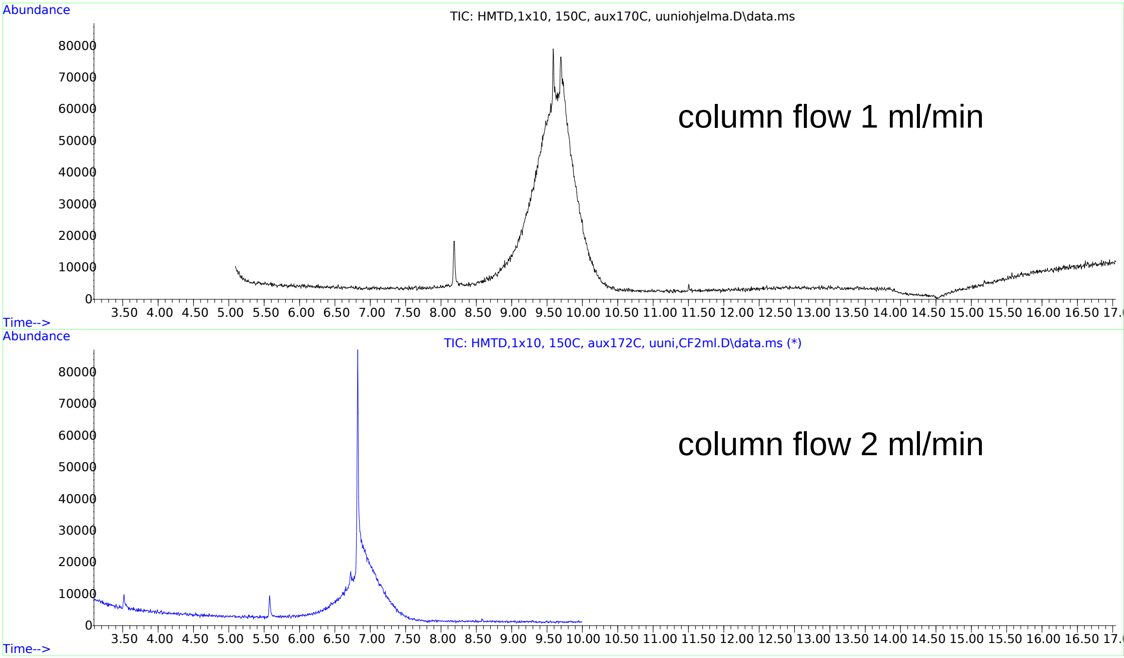


Figure 18: The effect of carrier gas column flow on HMTD peak shape, column = 30 m HP-5MS

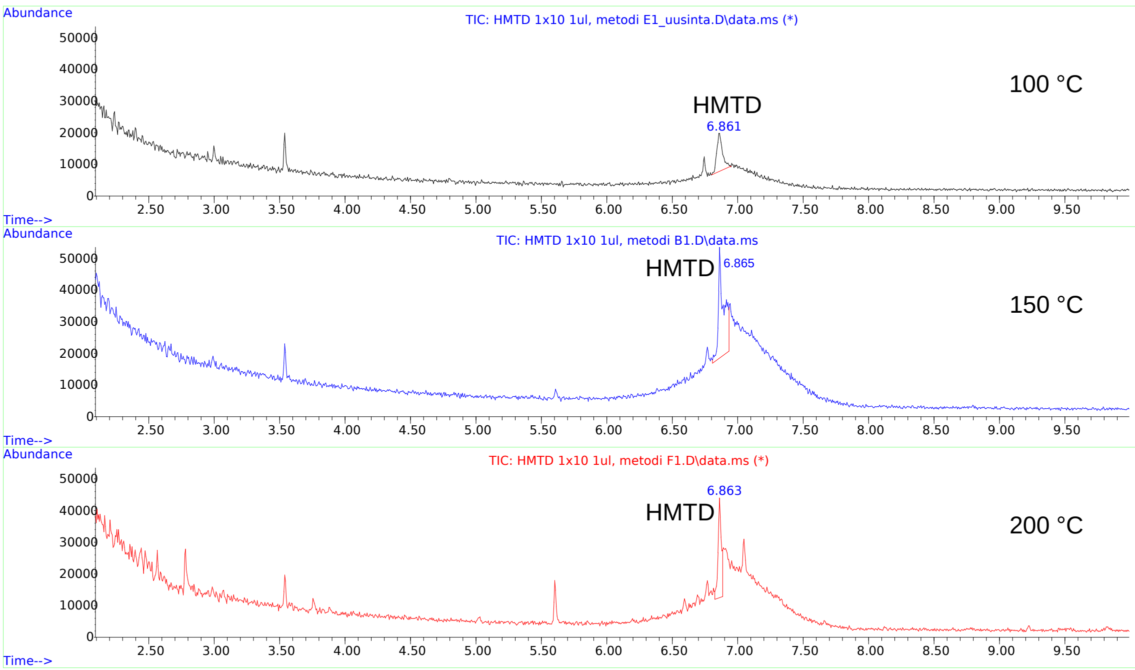


Figure 19: The effect of inlet temperature on the GC/MS analysis of HMTD, peak heights were as follows: 12042 (100 °C), 33140 (150 °C) and 29767 (200 °C)

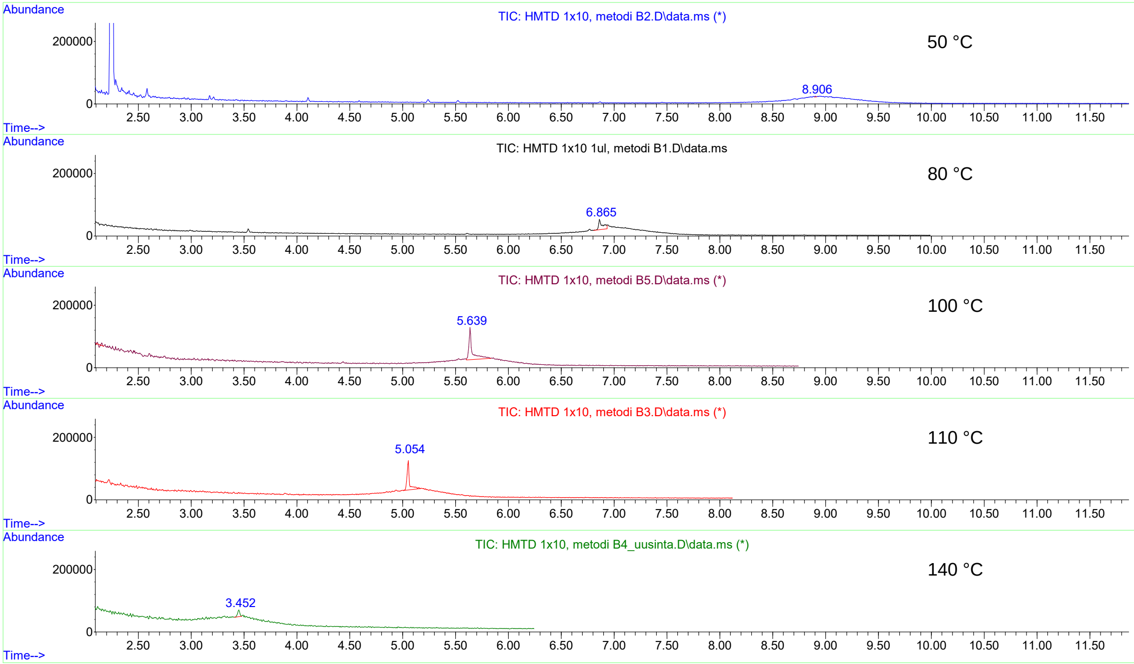


Figure 20: The effect of initial temperature of the column oven on the GC/MS analysis of HMTD

Table 8: Results of the initial temperature of the column experiments with HMTD

$T_{\text{oven,initial}}$ °C	t_{RT} min	I_{peak}	A_{peak}	notes
50	8.906	-	-	no peak
80	6.865	31366	816115	very small peak, nearly lost due to broadening
100	5.639	98720	2263458	-
110	5.054	91810	1506986	-
140	3.452	20642	305178	very small peak, nearly lost due to broadening

Impact of the column length on the HMTD GC analysis was studied with both columns. The shorter column shortened the retention time of the peroxide by approximately 2.5 minutes and yielded nearly 9 times higher signal. Despite of the better signal feedback level with the shorter column, it produced noticeably worse mass spectrum for the analyte. Library search match quality number fell from 90 to approximately 50. Also, a significant change in the mass spectrum was observed with the shorter column: intensity reduction of the heavier fragments and change in relative heights of the lighter ones. Thus, the shorter column would be recommended due to its better signal level, but further experiments would be needed to study whether the mass spectrum qualities could be enhanced with it. Corresponding results are shown in Figure 21.

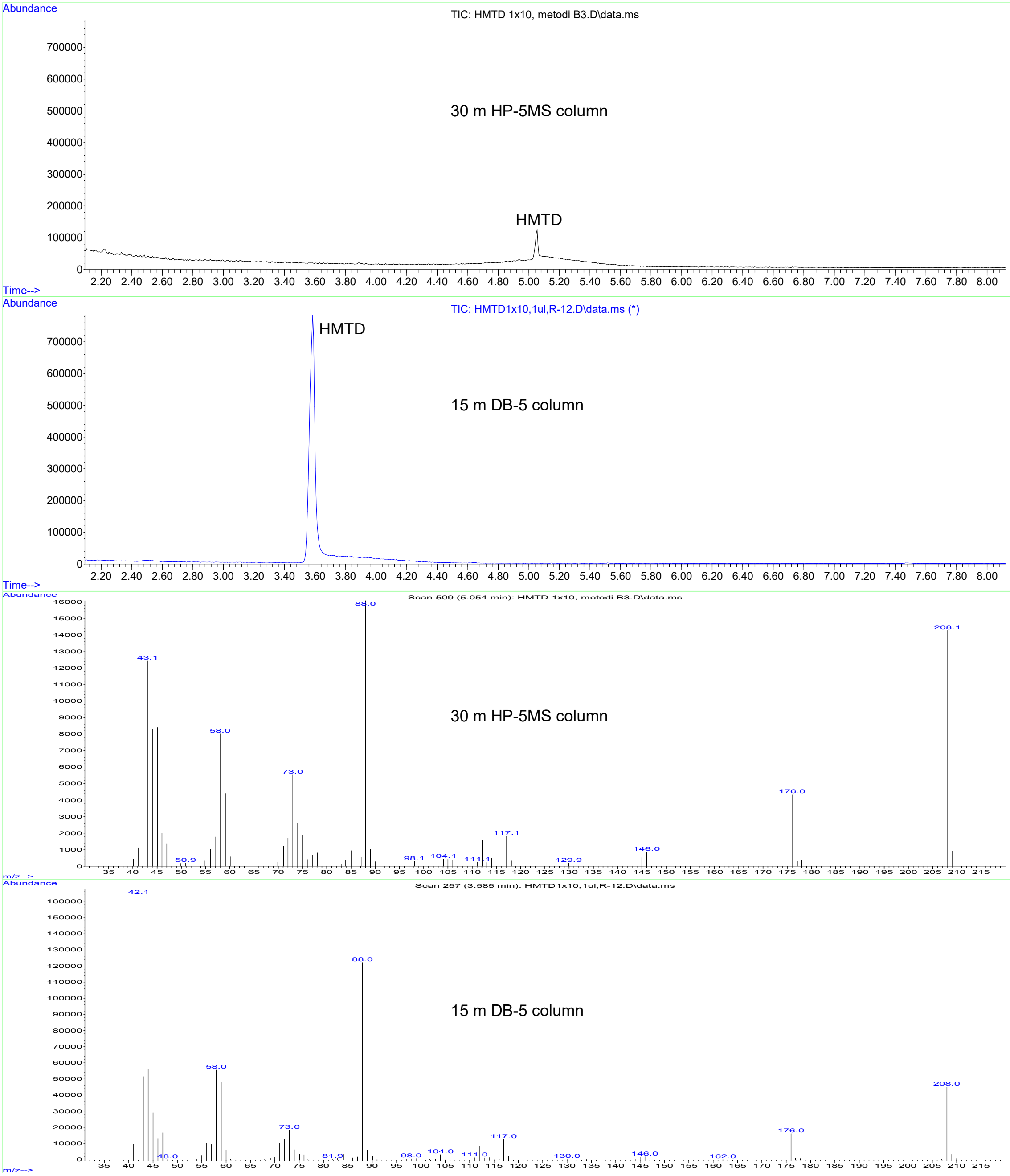


Figure 21: The effect of the column length on HMTD GC analysis, peak heights were approximately as follows: 89000 (30 m HP-5MS), 770000 (15m DB-5)

Thermodesorption sample introduction experiments with SBSE Twister technique for HMTD were unsuccessful. No peaks could be detected in the chromatograms when HMTD-acetone solution was spiked on a Twister and then analysed with thermodesorption GC/MS technique. Any parameter combination did not seems to produce encouraging results in favor of HMTD thermodesorption from SBSE sorbent rods. For this reason, SPME fiber was tested for the sample introduction instead. HMTD-acetone solution was spiked directly onto the SPME fiber, although difficult in practice, it gave hope for the sample injection method. A distinct peak could be observed following 2 µl spiking of the 50 µg/ml (1:10 dilution of the stock solution) HMTD in acetone solution onto the fiber. It should be noted thought, that nearly a 14-fold reduction in signal feedback intensity was observed, compared to the liquid injection of the acetone solution. The result might still hint something about possibilities of the sampling method. Figure 22 shows the chromatogram and mass spectrum of the SPME spiking thermodesorption analysis. Mass spectrum quality of HMTD injected with thermodesorption was relatively good, suggesting no extensive thermal degradation was present. These results were obtained with parameters shown in Table 9.

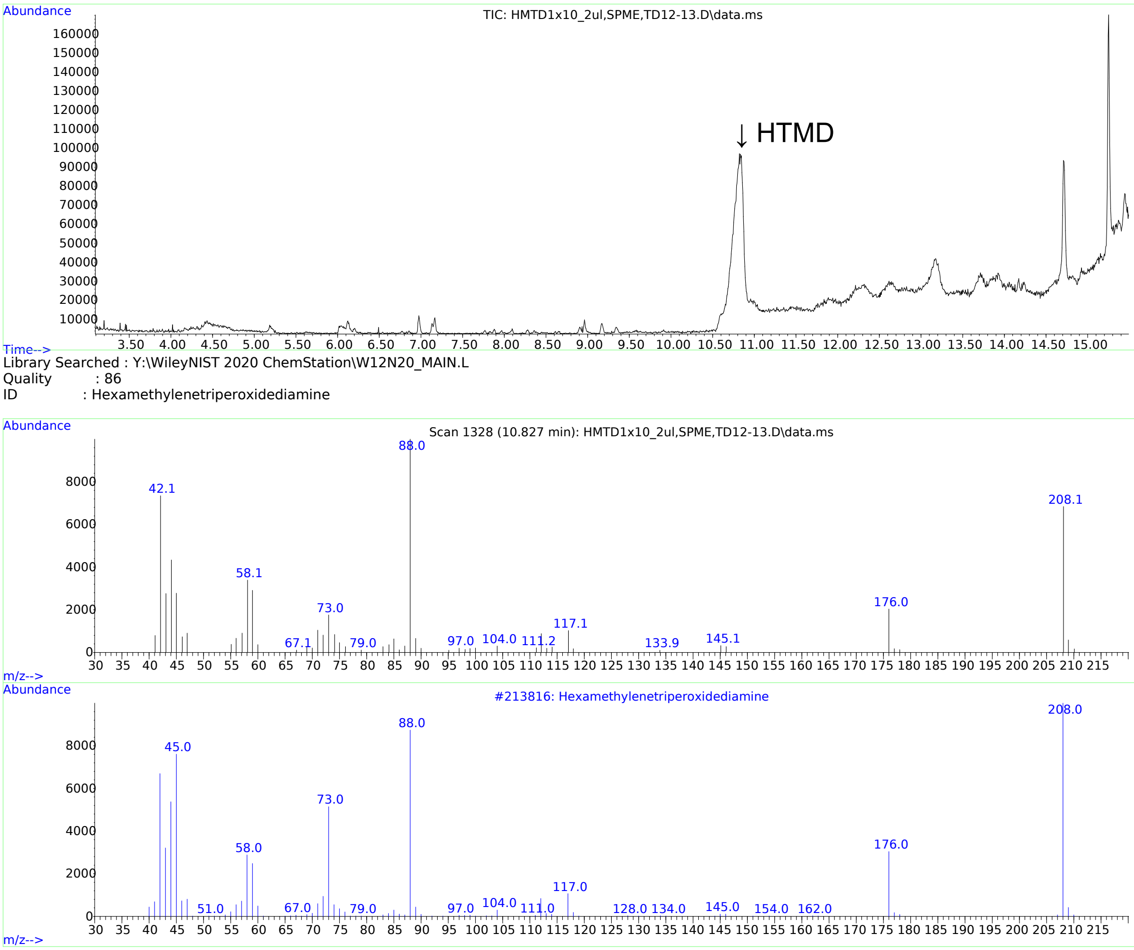


Figure 22: Analysis result of HMTD spiked onto an SPME fiber (injected with thermodesorption), *above*: chromatogram of thermodesorption run of SPME fiber spiked with HMTD acetone solution, peak height: 87000, *below*: mass spectrum library search result of the HMTD peak, the search result showing relatively good mass spectrum quality and library search match value of 86

To verify the assumptions of HMTD thermal degradation in the thermodesorption phase of the SBSE technique, a test was conducted, where acetone dilution of HMTD

Table 9: Parameters of HMTD spiked SPME thermodesorption analysis

parameter	value
inlet liner type	narrow liner
column	15 m DB-5
T_{TD}	150 °C
t_{TD}	1 min
$T_{\text{oven,initial}}$	40 °C
$T\ t^{-1}_{\text{oven}}$	16 °C/min
T_{aux}	170 °C
cryotrapping	no

was spiked onto the surface of a microvial glass tube. The aforementioned microvials are meant for pyrolysis analyses with the Optic 4 inlet system. The idea was, that with bare glass surface, the effect of the analyte binding to the sorbent material is avoided. By this practice, it could be proved which part of the sample introduction was the most significant obstacle. 2 µl of the 50 µg/ml (1:10 dilution of the stock solution) HMTD in acetone solution was spiked onto the vial's outer surface. The results showed that HMTD could be analysed by thermodesorption from a bare glass surface. Thus it must be understood that HMTD is very challenging to work with thermal desorption sample introduction. Corresponding analysis results are shown in Figure 23.

Headspace sample collection was attempted with the SPME technique after initial success with the thermodesorption technique. In order to do so, 5 µl of the 50 µg/ml HMTD in acetone solution was injected into a 40 ml headspace vial and was closed with a PTFE septum cap. Headspace sampling was performed for 30 minutes in 60 °C, due to the low vapor pressure of the HMTD. A substantially small signal for the analysis was observed with extremely poor sample recovery efficiency (Figure 24). The thermodesorption and other instrument parameters are shown in Table 9.

Finally, the effectiveness of the cryotrap focusing was tested for HMTD. The results clearly showed, that the recovery of HMTD was much worse with cryotrapping. Presumably the analyte cannot handle two high temperature shocks, namely from the inlet at the sample introduction phase and the cryotrap releasing thermal shock, in addition to the heat stress of the chromatographic separation. Thus, according to these results, the use of the cryotrap is off limits for the HMTD or at least it demands rigorous further method development.

The SBSE method proved unsuitable for headspace sampling of HMTD at trace level. There was some success in gas chromatographic HMTD analyses from acetone solution, as well as with SPME thermodesorption sample introduction. The short-comings of HMTD headspace analyses are probably related to the extreme thermal sensitivity of the analyte and low vapor pressure. After all, headspace sampling exposes the samples to several heating cycles that might deteriorate the analytes. For possible future method developments, the SPME technique seems more promising over the SBSE technique. This phenomenon is probably due to slower phase transfer reactions with the bulky SBSE sorbent matrix compared to the small-mass SPME.

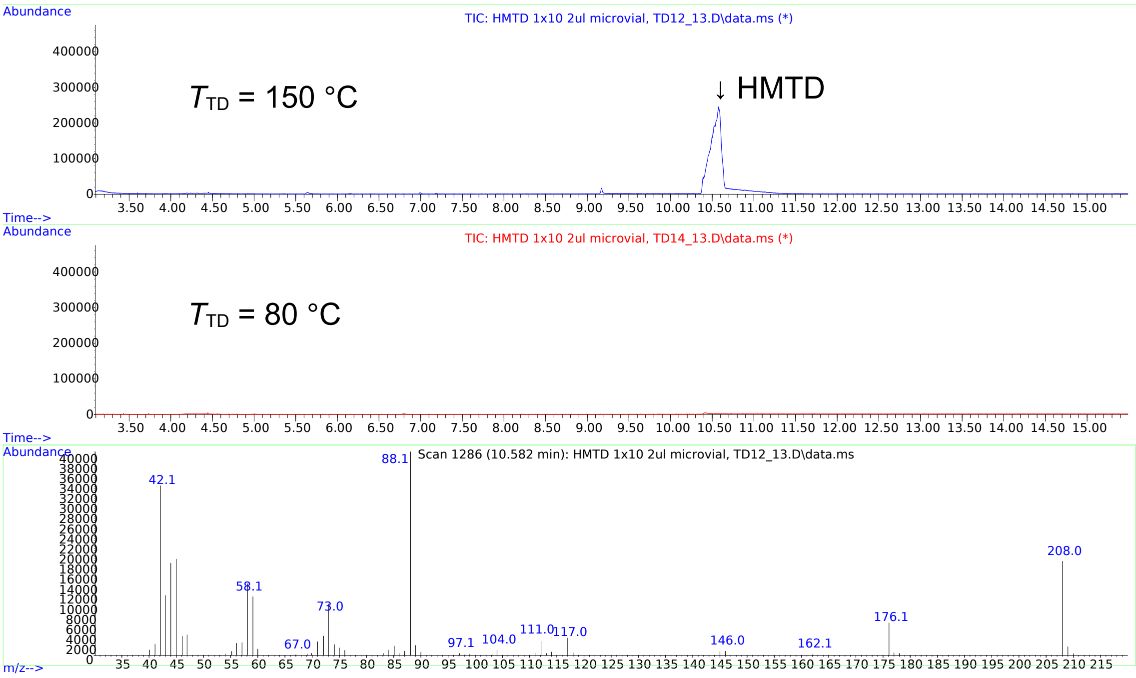


Figure 23: Results of the HMTD microvial spiking thermodesorption, *top*: thermodesorption chromatogram at 150 °C, *middle*: thermodesorption chromatogram at 80 °C, *bottom*: mass spectrum of the HMTD peak in the top chromatogram (T_{TD} = 150 °C) showing a good quality mass spectrum for the HMTD

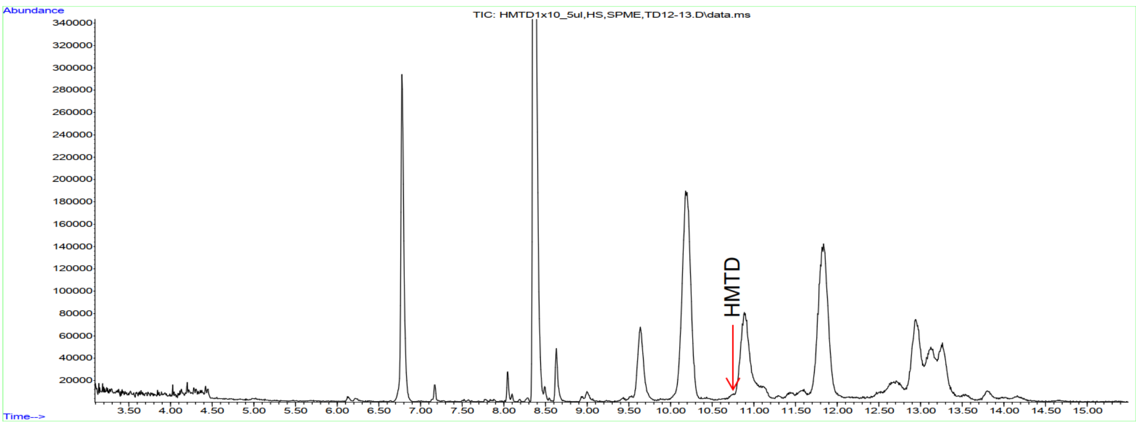


Figure 24: Chromatogram of SPME headspace sampling of HMTD

4.1.3 MEKP

The commercial MEKP solution was diluted in acetone by pipetting 5 µl of the product into a 10 ml volumetric flask. The flask was then filled with acetone, yielding a 0.05 % stock solution. Further dilutions in 1:10 and 1:100 ratios were then prepared of the stock solution in acetone. For each run on the GC/MS instrument, 1 µl of the dilution was injected with a manual injection syringe. Chromatograms of the analyses are shown in Figure 25. All of the analyses were performed on the 30 m HP-5MS column.

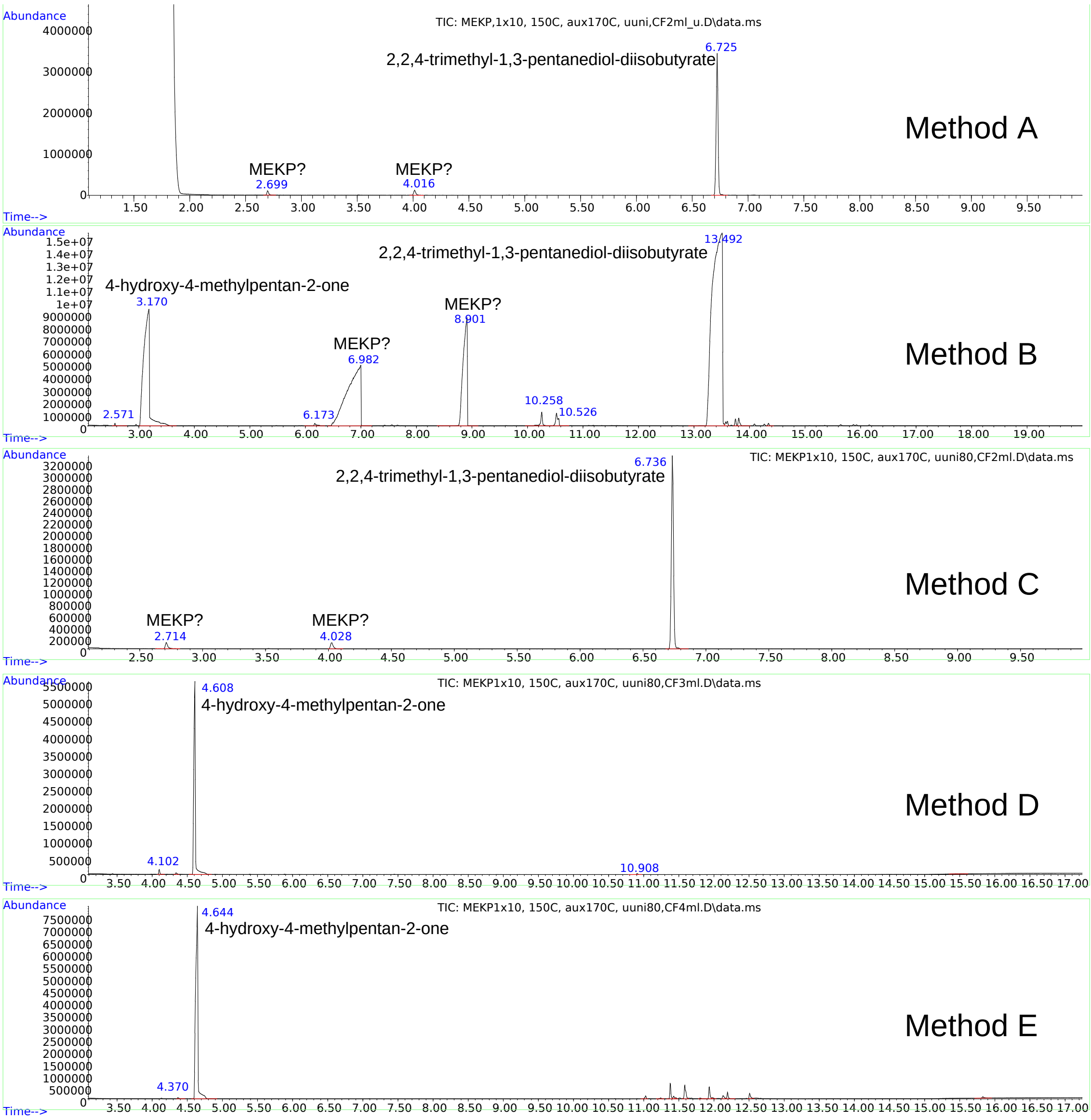


Figure 25: Analytical results for MEKP liquid injections by GC/MS, method names from A to E refer to Table 10, *note*: for Method B run 1 µl of the 0.05 % stock solution was injected and thus the peaks appear at higher intensity, for other runs 1 µl of the 1:10 acetone dilution of the 0.05 % stock solution was injected

Different parameters of the instrument used for the analyses are shown in Table 10. Each parameter change was performed after previous analysis was conducted. Before each injection, pure acetone was injected into the instrument and the cleanliness of the baseline was confirmed.

Table 10: GC/MS method parameters of MEKP liquid injections

parameter	method A	method B	method C	method D	method E
GC column	HP-5MS*	HP-5MS*	HP-5MS*	HP-5MS*	HP-5MS*
T_{inlet} (°C)	150	150	150	150	150
Q_{TCF} (ml/min)	2	2	2	3	4
$T_{\text{oven,initial}}$ (°C)	80	40	80	35	35
$T\ t_{\text{oven}}^{-1}$ (°C/min)	16	10	16	20	20
T_{aux} (°C)	170	170	170	325	325
cryotrapping	no	no	no	no	no

* column length = 30 m

Analysis results of the MEKP on the GC/MS instrument were not quite unambiguous. The known by-products in the commercial MEKP product (2,2,4-trimethyl-1,3-pentanediol-diisobutyrate and 4-hydroxy-4-methylpentan-2-one) could be identified by their mass spectra with good reliability. The mass spectrum libraries gave satisfactory matches to them and their mass spectra were identical to those retrieved from the library. However, for peaks marked with *MEKP?* in Figure 25, the mass spectrum libraries were unable to give any good search results or matching mass spectra. The mass spectrum of each peak marked with *MEKP?* was practically the same with small variations. Such spectrum is shown in Figure 26.

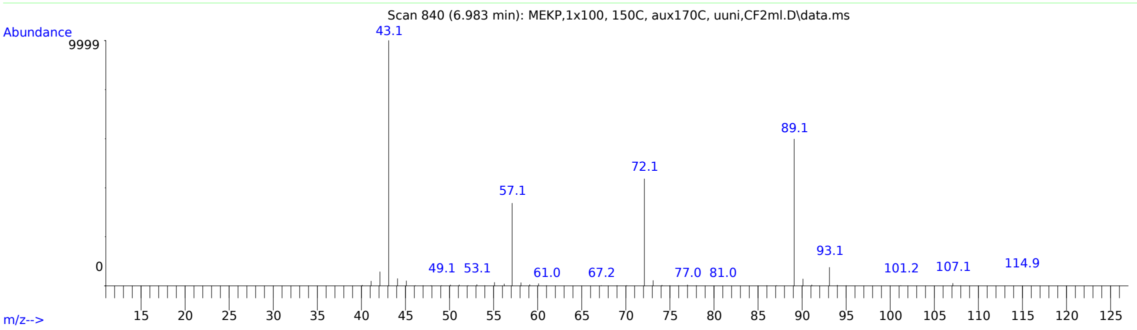


Figure 26: Acquired mass spectrum of suspected MEKP molecules of the liquid injection GC/MS analyses

The mass spectrum shown in Figure 26 does not match any of the additives in the commercial MEKP product. There is some level of resemblance to the EI mass spectrum of methyl ethyl ketone (MEK), also called 2-butanone. The primary fragments of MEK are m/z 72, 57, 43, 29 and 15, based on alpha-cleavage pathway of MEK. However, the sample mass spectrum shown in Figure 26 contains fragments, that cannot be explained by MEK EI fragmentation. Namely, fragment ions m/z 89 and 93. These two ions, on the other hand, are typical for MEKP, in addition to those fragments that are present in MEK too. Partial fragmentation patterns of MEK and MEKP are shown in Figure 27. The m/z 93 peak is presumably from fragment ion ($C_2H_5O_4^+$) [62].

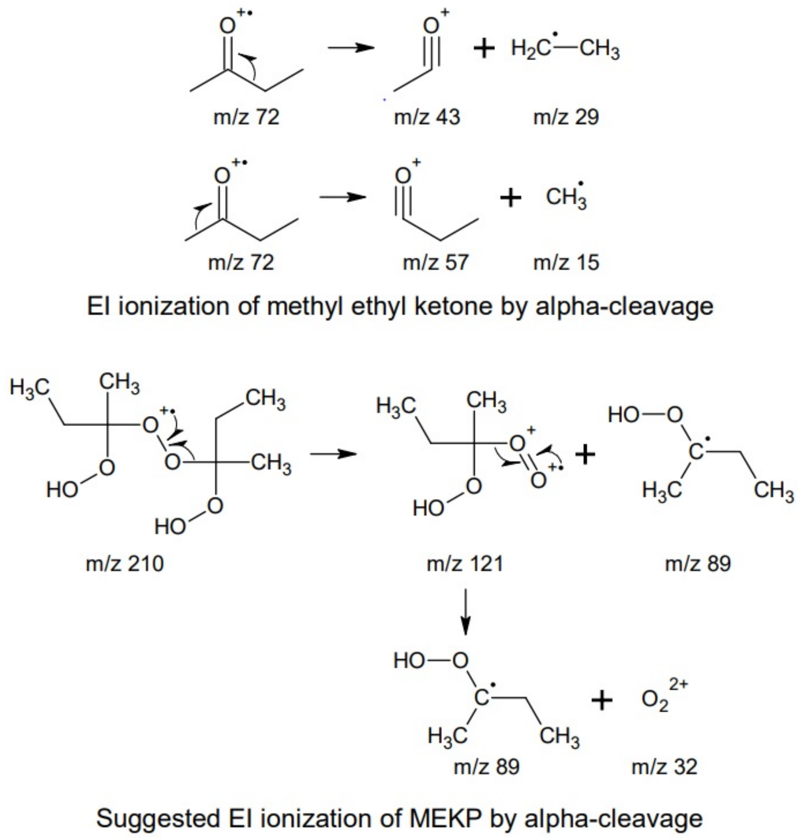


Figure 27: Above: known fragmentation pattern by EI ionisation of MEK, below: suspected fragmentation via alpha-cleavage of MEKP dimer from the molecule ion, producing mass fragments m/z 121, 89 and 32

However, it is not confirmed that the observed peaks in the chromatograms were actually from MEKP. Lack of reference data sets difficulties to verify the results. Simulated mass spectra of MEKP seems to support the hypothesis [62], as does some analytical results to a certain degree also [39].

As can be seen from the chromatograms shown in Figure 25, the GC/MS analysis of MEKP is not quite straightforward. The largest problem seems to be, that many of the co-products of the commercial MEKP product were much more abundant in the mixture than the actual MEKP. According to the safety data sheet of the product, the MEKP should, however, be the primary compound of the mixture. Such result could be, for example, due to thermal degradation of the peroxide during the analysis.

Due to the encountered issues with weak repeatability and seemingly low quality of the mass spectra, analyses with MEKP were not continued to the headspace trace analysis phase. Limited time during the method development project did not allow further efforts to be put towards the troubleshooting of the MEKP GC/MS analysis. On the other hand, the chromatographic analysis of MEKP was not considered as a priority for method development compared to the two other peroxides at this time.

4.1.4 Emulsion explosives

Capabilities of the SBSE headspace technique was tested with the solid explosive material directly. Approximately 5 g of the explosive material was placed into a 50 ml Erlenmeyer flask. An SBSE sorbent rod was placed into the flask which was then closed with a ground glass stopper. Headspace sampling was carried out at 100 °C for 30 minutes. The same procedure was conducted for both: Forcit Kemix and Forcit Kemix-A. Analysis parameters are shown in Table 11.

Table 11: Parameters of the emulsion explosive headspace analyses

parameter	value
inlet liner type	fritted liner
column	15 m DB-5
l_{Twister}	20 mm
V_{HS}	50 ml
T_{HS}	100 °C
t_{HS}	30 min
T_{TD}	210 °C
t_{TD}	3 min
$T_{\mathrm{oven,initial}}$	35 °C
$T\ t^{-1}_{\mathrm{oven}}$	20 °C/min
$T_{\mathrm{oven,final}}$	250 °C
T_{aux}	325 °C
cryotrapping	yes
$T_{\mathrm{cryo,low}}$	−30 °C
$T_{\mathrm{cryo,high}}$	210 °C

The results indicate that the headspace sampling has some capability of collecting the hydrocarbon component of the emulsion explosive bulk material. For both of the tested products, the analysis could detect n-alkanes ranging from C14 up to C26. However, the sample recovery efficiency was not especially good, considering the large amount of sample used for the headspace sample collection. Additionally, the hydrocarbon profile of the sample acquired with the headspace collection was not very clear. The range of n-alkanes indicate presence of fuel oil and paraffin wax in the emulsion explosives. Paraffin waxes typically consist of n-alkanes roughly between C19 and C35. Typical n-alkane range of fuel oils is typically approximately from C8 up to C33. Especially for Kemix A it appears that the product contains paraffin wax, as distinct pattern of n-alkane homologous series can be seen resembling a normal distribution of the peak intensities around C23. Total ion chromatograms and extracted ion chromatograms of the emulsion explosives are shown in Figure 28.

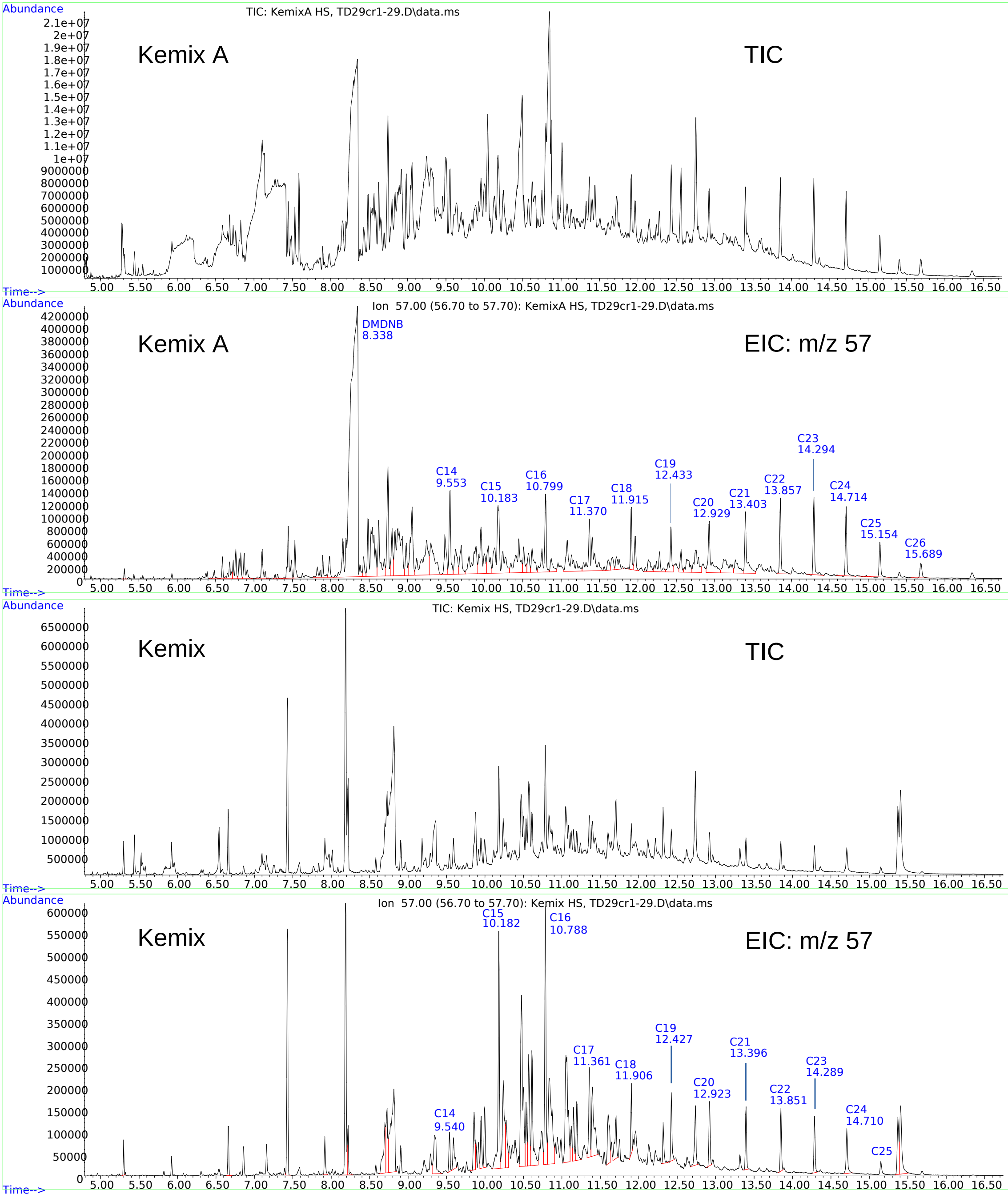


Figure 28: Results of HS/GC/MS analyses of emulsion explosives, total ion chromatograms (TIC) and extracted ion chromatograms (EIC) for m/z 57 shown for both Kemix and Kemix A products

One interesting feature of the headspace GC/MS analysis of emulsion explosives was the finding of 2,3-dimethyl-2,3-dinitrobutane (DMDNB) in Kemix A. In the other emulsion product (Kemix), DMDNB was not detected. DMDNB is a volatile organic compound used in particular as a taggant in explosives. [63, p. 175]. Taggants are special marker molecules that are mixed into explosive materials during the manufacturing phase in order to aid analysis and detection of explosives. DMDNB is a very common taggant compound, mainly because specially trained canines can detect its vapors in air in very low quantities.

Compared to a n-heptane solution of the emulsion explosives analysed with a dedicated hydrocarbon analysis GC/FID method, the headspace chromatogram is of significantly lower quality. The dedicated hydrocarbon analysis method produces a very clear paraffin wax profile for the bulk material, unlike the SBSE headspace sampling. The results are fairly consistent with the general consensus that heavy hydrocarbons are poorly compatible with headspace. For comparison, a GC/FID chromatogram of the Kemix A n-heptane extract is shown in Figure 29.

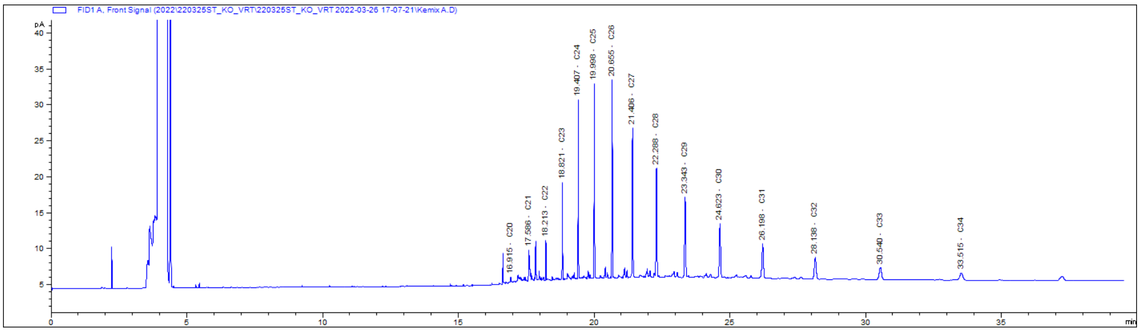
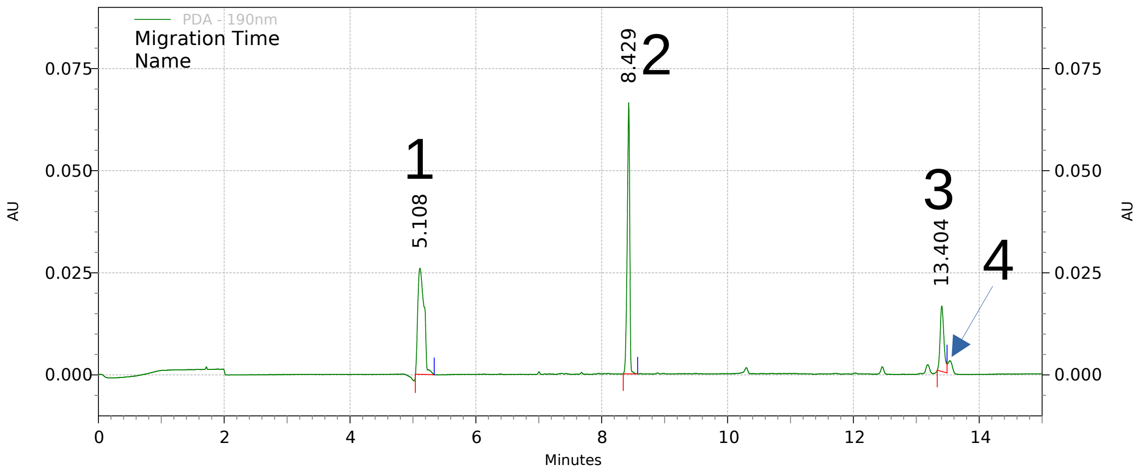


Figure 29: Chromatogram of Kemix A n-heptane extract analysed on GC/FID with dedicated paraffin wax method

4.2 CE/DAD method development

Analysis experimenting with TATP with CE technique was started by weighing 3.2 mg of powdery TATP into a 10 ml volumetric flask. The flask was then filled with 10 % (volume concentration) of acetone in distilled water solution. The mixture was then sonicated in ultrasonic bath for 20 minutes. The mixture was finally filtered with 0.45 µm syringe filter. An observation was made, that all of the TATP was not dissolved in the given acetone-water solution. Prepared TATP solution was then analysed with the CE instrument using parameters shown in Table 5 (with 25 kV). Test mix solution provided with the analytical MEKC electrolyte kit was used as a reference sample. The test mix analysis showed that the instrument and the method were functioning as expected, even though separation of tryptamine and sulconazole was observed to be worse than specified by the analytical kit manufacturer. An example of a test mix run is shown in Figure 30. Analytical runs of TATP solution did not produce any other peaks than the EOF in the electropherogram.



PDA - 190nm
Results

Name	Migration Time	Area	Height	Resolution (USP)	S/N (ASTM)
	5.108	181721	25983	0.00000	59.440351
	8.429	182710	66362	26.90495	237.715187
	13.404	70331	15978	53.71921	21.249368

Figure 30: Electropherogram of the MEKC analytical kit test mix run (used separation voltage: 25 kV), *1*: EOF and dimethylformamide, *2*: phenylacetic acid, *3*: tryptamine, *4*: sulconazole

In efforts to get any result of TATP with the CE method, a stronger solution was prepared. This time weighing 10 mg of the TATP powder into a 10 ml volumetric flask. The flask was filled with 20 % (by volume) of acetone in distilled water solution. Again, after sonication, undissolved TATP was observed on the bottom of the flask.

The stronger TATP solution did not produce different results: no peaks were observed for the TATP solution samples.

Next, analyses were attempted with higher separation voltage (30 kV), in case the migration time of the TATP was unexpectedly high. The same TATP sample of 10 mg of TATP in 10 ml of 20 % acetone-water solution was used. Results remained the same, no peaks were observed. One observation was, however, that the TATP sample exhibited a larger EOF peak than the runs of the test mix sample. The phenomenon could be due to the analytes migrating out of the capillary simultaneously with the EOF and thus causing a larger signal. This hypothesis was proved false by preparing identical samples of the acetone-water solution used for the TATP samples, but without the TATP. These solvent samples also exhibited larger EOF peaks compared to the test mix samples. The height of the EOF peak in the test mix sample runs was on average at 0.04 AU level (AU = absorbance units). The heights of the EOF peaks in the TATP and solvent sample runs were on average at 0.25 AU level.

Another observation was that within the sequence runs of the test mix samples with the MEKC CE method, the quality of the analysis results started to degrade. In the beginning of a sequence, resolution between the analytes was at least satisfactory. However, at the end of the sequence runs, resolution of especially tryptamine and sulconazole was dramatically worse. Such situation is illustrated in Figure 31. Deterioration of resolution is assumed to be due to ionic balance and capillary surfacing treatment wearing out during analyses.

To further increase the TATP concentration in the solutions, to compensate for the weak UV absorption of it, 25 mg of TATP was weighed into a 10 ml volumetric flask. The flask was then filled with pure acetone. Of this solution, dilutions were then prepared using the MEKC kit accelerator solution as diluting agent. Solutions with dilution factor of 1:2 and 1:5 were prepared. As blank samples, solutions of pure acetone were prepared by diluting it with the MEKC kit accelerator solution by dilution factor of 1:2 and 1:5. This time, unidentified extremely small peaks were detected in the electropherograms of the TATP samples. These peaks were not present in the blank sample runs. Summary of the results is shown in Figure 32. The peaks are possibly from the TATP.

The results presented above do not show good analytical quality for TATP. Observed peaks were extremely small and their signal-to-noise ratios were poor. To achieve the shown results, samples with very high concentration had to be used. The concentrations of the TATP solutions used, were well above those expected from a trace analysis method. Also, it is not confirmed that the peaks were from TATP, as optical detection of the CE method does not have characterisation capabilities. The migration time for suspected TATP was a tad over 6 minutes. This observation seems to in line with literature results of TATP migration time acquired with CE-MEKC technique, where migration times with shorter capillary ranged from 2.4 to 4.2 minutes. Concentration of SDS significantly affected the migration times, with correlation that higher SDS concentrations delayed the migration time of TATP [20].

Finally, experiments were conducted similarly as described previously, but instead of diluting the TATP-acetone solutions with the MEKC kit accelerator solution, the dilutions were made in distilled water. Thus 25 mg of TATP in 10 ml of acetone

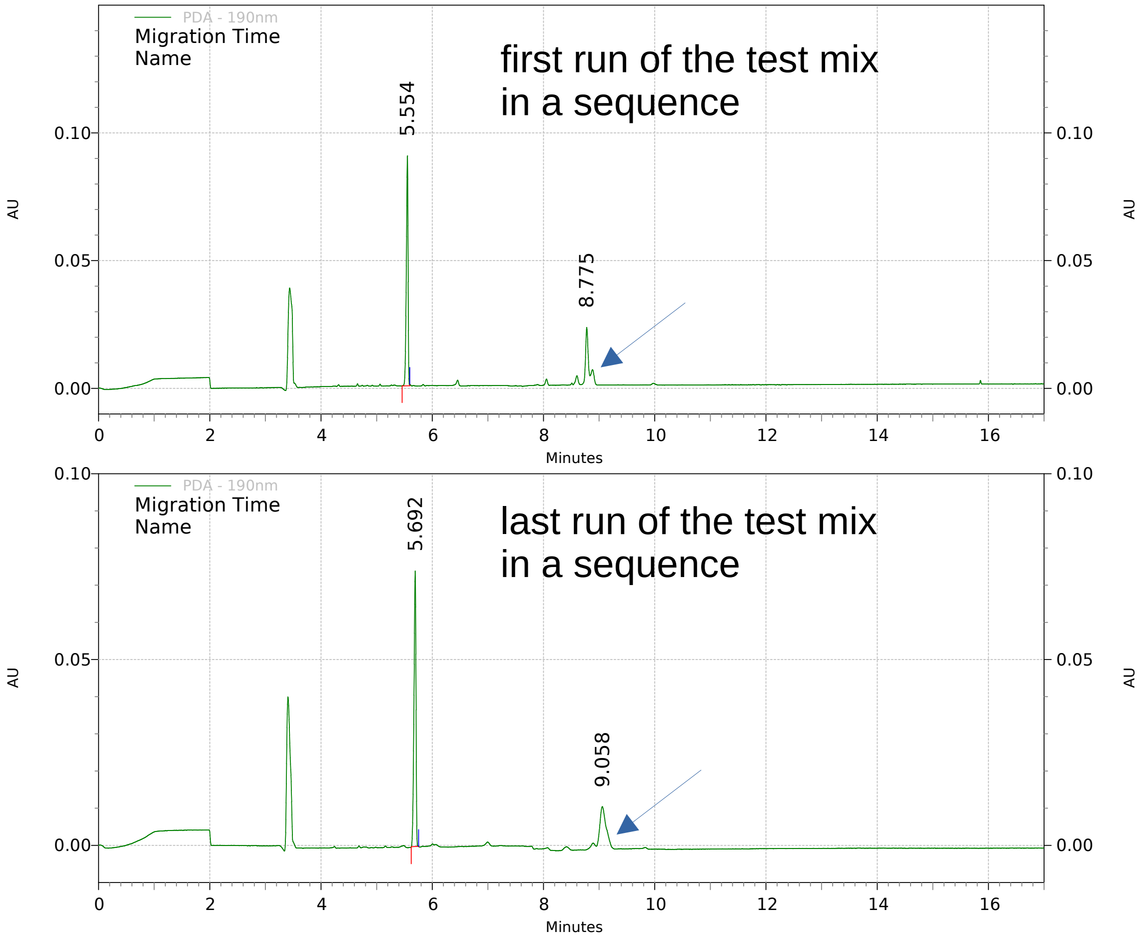


Figure 31: CE method resolution decrease during sequence runs with the MEKC method, weaker resolution of tryptamine and sulconazole in the later run highlighted with an arrow

was diluted with water in 1:2 and 1:5 ratios. Equivalent blank samples were also prepared. For these analyses, significant instability of the instrument was observed. For many runs, not even the EOF peak was detected, indicating of an electrophoretic problem with the analyses. Some runs exhibited a very turbid baseline. The test mix reference samples were analysed without any problems indicating that there were no issues with the instrument. Possibly, the critical micellar concentration was off, due to the large amount of acetone in the samples. No useful data could be achieved of the runs.

Significant difficulties were encountered with CE analyses of the peroxides. The most notable drawbacks were strong hydrophobicity of the peroxides and their lack of UV absorption. The CE technique depends on water-based buffer and electrolyte solutions, which effectively denies the possibility to analyse hydrophobic analytes. Another issue was related to the detection method – UV absorption. As the MEKC electrolyte kit that was used, is based on direct detection, it is required that the analytes would have UV absorption. But as is in the case of the peroxides, they

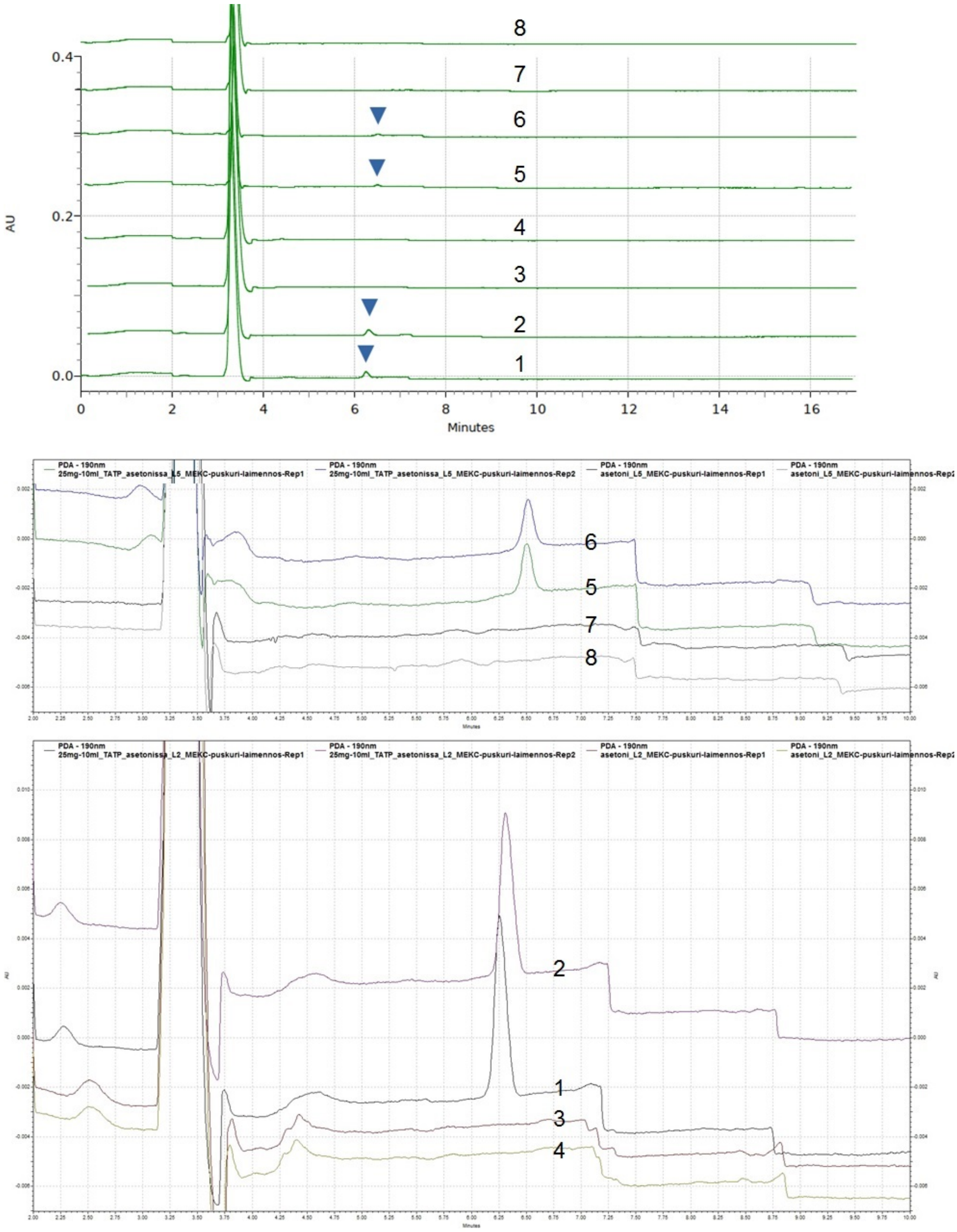


Figure 32: Electropherograms of the TATP-acetone solutions diluted with the MEKC accelerator solution, *1*: 1:2 dilution of TATP (run 1), *2*: 1:2 dilution of TATP (run 2), *3*: (blank) 1:2 dilution of acetone (run 1), *4*: (blank) 1:2 dilution of acetone (run 2), *5*: 1:5 dilution of TATP (run 1), *6*: 1:5 dilution of TATP (run 2), *7*: (blank) 1:5 dilution of acetone (run 1), *8*: (blank) 1:5 dilution of acetone (run 2), *note*: arrows highlight the observed small peaks; the three graphs are at separate scales

only have weak UV absorption or no absorption at all. This creates a challenging equation between the concentration of the analytes and their weak signal feedback.

5 Conclusions

The goal of this thesis was to develop analytical methods to facilitate analysis of organic peroxides and emulsion explosives. This goal was at least partially fulfilled. A viable method for analysis of bulk and trace samples of TATP was achieved. The capability to analyse TATP samples was set as a priority. As this goal is achieved, the ability of the forensic laboratory to investigate potential incidents has improved. Presented method was granted an accreditation status by Finnish Accreditation Service (FINAS) and the method was deployed in service in the laboratory. Complete method with recommended parameters is shown in Appendix B.

GC/MS analysis of HMTD proved to be challenging. Optimal parameters for its bulk analysis were successfully found. It is uncertain whether the problems encountered in headspace sampling were more related to the low volatility of the peroxide or whether optimal parameters were simply not found. One possibility could be to study if it is possible to extract HMTD residues from miscellaneous debris materials with acetone and analyse HMTD as a liquid injection from the acetone extract. For this practice, LODs of the methods should be first determined to verify its suitability for trace analysis. Another possibility would be to develop further the SPME sample collection method, as it exhibited some promising results.

It was shown that GC/MS analysis of MEKP with given instrumentation and materials is not simple. Some uncertain results were obtained, which can be used to guide future method development. Indeed, if a GC/MS method is to be used for analysis of MEKP, considerable amount of further work is still needed. However, there is evidence that already existing, fast, simple and effortless analysis methods for MEKP already exist. Namely Raman spectroscopy has been proved to be very effective and possibly the easiest method available for such analytical activity [26, p. 20]. Of course, other techniques must be introduced and developed for the trace analysis purposes of MEKP, as simplest handheld spectroscopic methods are not suitable for trace analysis.

Naturally, the most desirable situation would be that all three peroxides could be analysed with the same method. In many cases, samples from explosion incident site are unique and they can only be analysed once. Additionally, if other common explosive substances could be included in the method, it would be very useful and a powerful analytical tool. With further method development based on the results obtained in this work, it might be possible to develop a suitable HS/GC/MS method for this purpose. While on the other hand, LC/MS technique has its undeniable strengths and might be more suitable for analysis of delicate peroxides. It also has been speculated that the lifetimes of analytical columns may be exceptionally short for organic peroxide analyses with gas chromatography [16].

Headspace analysis of emulsion explosives does not seem very lucrative. The main components of these explosives are principally compounds with a relatively high boiling point. For such compounds, headspace sampling is not the optimal technique. Instead, it could be beneficial to investigate how well dedicated gas chromatographic oil analysis methods would be able to detect emulsion explosive residues. It is known that such methods have very low LODs and that they can provide extremely detailed data about the hydrocarbon composition of samples [64]. However, an interesting result of the HS analyses of emulsion explosives was the detection of a taggant substance. One possibility is, that the headspace method could be used in parallel to the dedicated oil analysis methods. Finding an explosive material taggant compound in an explosive residue sample would certainly be valuable information in forensic investigation. Of course, further experiments are needed to verify detection limits for such procedures.

Analytical performance of the capillary electrophoresis system with absorbance detection for the analysis of organic peroxides was not excellent. Presumably the problem was due to two main reasons. Firstly, the peroxides are insoluble in water, and thus in aqueous buffers. The second reason is the lack of UV absorption of the peroxides. The latter reason could possibly be solved by doping the analytical buffer solutions with chromophores and by modifying the method to implement indirect detection, or preferably using completely different type of detector in the CE system. On the other hand, neither the solubility issue would not catastrophical, if low enough LOD for the method could be reached. In a qualitative method, exhaustive extraction of the analyte from sample might not be necessary, because concentration is not the primary consideration. Also, other solvents besides acetone could be tried. The CE method might still have undiscovered potential for the analysis of the peroxides. After all, excellent results have been achieved with it in literature [20].

The results obtained in this work provide the laboratory with new information that was not previously available. This new information can be used to design new approaches for further development of residue analysis of explosives. The results can also be used as a basis for possible further method development undertakings.

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A Summary of parameter optimisation data for TATP

Table A1: TATP as acetone dilution manual liquid injection, retention time repeatability with 15 m DB-5 column, (SD = standard deviation, max-min = difference between largest and smallest retention time value)

repetition	t_{RT} min
1	5.826
2	5.813
3	5.807
4	5.807
5	5.817
6	5.815
mean	5.815
SD	0.00649
max-min	0.0190

Table A2: Effect of the cryogenic trapping on liquid injection of TATP, TATP acetone dilution manual liquid injection with 15 m DB-5 column

trapping	t_{RT} min	I_{peak}	$I_{\mathrm{peak}}/I_{\mathrm{max}}$ %	A_{peak}
yes	6.173	522105	100	6238000
no	6.147	414858	79	6431865

Table A3: Effect of thermodesorption temperature of TATP from Twister sorbent rod, TATP as acetone dilution spiked onto 10 mm Twister

T_{TD} °C	t_{RT} min	I_{peak}	A_{peak}	notes
70	-	-	-	no peaks
110	8.081	13400	495500	no interference
150	8.068	43350	2105400	no interference
210	8.068	61100	2301000	little interference
250	8.066	86900	2391900	significant interference

Table A4: Effect of thermodesorption time, TATP as acetone dilution spiked onto 10 mm Twister

t_{TD} min	t_{RT} min	I_{peak}	A_{peak}
3	8.066	65700	2662100
5	9.937	58000	2077500

Table A5: Effect of transfer column flow during the thermodesorption phase, TATP as acetone dilution spiked onto 10 mm Twister

Q_{TCF} ml/min	t_{RT} min	I_{peak}	A_{peak}
1	7.523	403000	4302460
2	7.524	424150	3908500
4	7.528	465900	5036500

Table A6: Comparison of the efficiency of sample recovery by thermodesorption with liquid injection, TATP as acetone dilution spiked onto 10 mm Twister (1 µl), liquid injection volume: 1 µl

sample introduction method	Q_{TCF} ml/min	I_{peak}	I_{peak}/I_{max} %
thermodesorption	1	403050	93
thermodesorption	2	423500	98
manual liquid injection	-	432800	100

Table A7: Effect of cryogenic trapping on thermodesorption sample introduction, 1 µl of 5 µg/ml TATP solution injected into a 50 ml Erlenmeyer flask, headspace collection: 30 minutes at 60 °C, 10 mm SBSE rod

trapping	$T_{cryo,low}$ °C	$T_{cryo,high}$ °C	I_{peak}	I_{peak}/I_{max} %	A_{peak}
no	-	-	38300	22	1784240
yes	-30	100	160000	94	-
yes	-30	210	170900	100	1446000

B Method parameters for GC/MS trace analysis of TATP

Table B1: Recommended parameters for the SBSE headspace GC/MS trace analysis method of TATP

parameter	value
carrier gas	helium
inlet liner type	frit liner
SBSE sorbent rod length	2 cm
analytical column	15 m × 0.25 mm × 0.25 µm (film) DB-5
headspace sampling temperature	40 °C
headspace sampling time	$30 - 60$ min
inlet mode	splitless
inlet initial temperature	40 °C
inlet final temperature	210 °C
inlet heating rate	12 °C/s
inlet purge flow	2 ml/min
inlet purge time	1 min
inlet purge type	splitless
thermodesorption time	3 min
carrier gas column flow	1 ml/min
column oven initial temperature	35 °C
column oven final temperature	200 °C
column oven heating rate	20 °C/min
MS transfer line temperature	230 °C
mass spectrometer mode	SIM/scan
scan range	m/z $40 - 300$
SIM ions	m/z $75, 101, 117, 222$
cryotrapping	yes
cryotrap low temperature	-30 °C
cryotrap high temperature	100 °C
cryotrap heating rate	60 °C/s