

Optimization of SPME for determination of nitro compounds using GCMS

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Abstract:

SPME is extraction technique, which is compatible with gas chromatography. The sensitivity may be good for determination of very low concentration levels. In this paper is this method used for determination of aromatic nitro compounds. Mixtures of aromatic nitro compounds and concentrated nitric acid are potentially useful as improvised explosive devices. Therefore, it is necessary to find sensitive analytical procedures for the determination of residues after the explosion. Connection gas chromatography with mass detector was used for analysis. It is necessary to optimize conditions SPME (time, temperature, sorption and any amount of NaCl). To optimize the use of statistical techniques DEO. Suitable extraction conditions were found with this method. These conditions were tested on real samples after the explosion.

Keywords: SPME; GC-MS; aromatic nitro compounds

1 Introduction

In recent decades, improvised explosive devices (IEDs) have become an increasing topic of public concern, with high-profile incidents such as the Bali (2002), London transport (2005), Boston Marathon (2013) and Brussels (2016) bombings garnering mass international attention. Although the majority of media coverage has focused on large-scale incidents, there has also been a rise in explosive incidents involving smaller devices such as pipe bombs. This is particularly the case in the United States, where pipe bombs are considered to make up the vast majority of IED encounters [1]. These devices can be easily constructed from everyday materials, and the containment provided by the pipe can produce a large explosive effect using readily obtained low explosive powders such as black powder, black powder substitutes (e.g., Pyrodex and Triple Sevens) and smokeless powder [2].

A common sampling method for explosive residues, particularly on large, non-porous surfaces, is the use of swabbing techniques. A number of studies have thus evaluated various swabbing materials, solvents or extraction procedures in the recovery of both organic and inorganic explosives [3–6]. The findings of these studies have been varied, with the best swabbing media and wetting or extraction solvents often differing according to the recovery surface or target analyte utilized [7, 8]. Investigations have also been conducted regarding the stability of explosive residues stored under different conditions. These inquiries have established that volatile explosives such as TATP may rapidly evaporate at room temperature, while nitro aromatics such as TNT are prone to photo-transformation if left exposed to light [9, 10]. Suitable storage conditions must be determined for such samples in order to preserve their evidential value.

2 Experimental

GC-MS analysis was carried out using a gas chromatography GC2010 Plus with mass spectrometric detector TQ 8030 (Shimadzu, Co., Kyoto, Japan). The GC-MS system was equipped with a capillary column Rtx-TNT (15 m x 0.15 mm x 0.25 μm film thickness, Restek, USA). Helium 5.0 (Linde Gas a.s., Prague, Czech Republic) was used as the carrier gas at a constant linear velocity of 30 cm/s. The injector and the ion source were maintained at 250 °C and 200 °C, respectively. The column temperature was programmed as follows: the initial temperature was 40 °C (3 min), and then increased at a rate of 10 °C/min up to 180 °C (1 min). The mass spectrometer was operated in the SIM mode and in the negative chemical ionization (NCI) mode. Autosampler AOC 5000 was used for SPME injection of samples.

Methanol (analytical grade, Sigma-Aldrich, Germany) was used as solvent. Acetone (analytical grade, Sigma-Aldrich, Germany) was used as received. Nitrobenzene (NB), 2,4-dinitrotoluene (2,4-DNT), 4-nitrophenole (4-NF), 4-nitroaniline (4-AN) and 1-nitroso-2-naphthole (NN) were used as standard (all Explosia a.s., CZ). Standard solution (2,4-DNT, NB, 4-NA, 4-NF a NN) was prepared in methanol. The concentration level was 400 mg/l. Solutions for calibration were prepared from this solution (1, 10, 25, 50 a 100 mg/l).

SPME fibres (50/30 μm DVB/CAR/PDMS, 65 μm PDMS/DVB and 100 μm PDMS) were tested for extraction of nitro aromatic compound. A central composite design was generated using Statistica CZ 10 software (StatSoft, CZ) to investigate the choice of amount of NaCl, extraction temperature and time as shown in Table 1. A face-centred CCD ($\alpha=1$) with 3 replicates of each central point was selected. This design was chosen as five levels. Analysis of the data was conducted using Statistica 10, optimizing the recovery of 2,4-DNT, NB, 4-NA, 4-NF a NN to a maximum by their GC-MS peak areas.

Table 1: Factors and levels tested for face-centred central composite design

<i>parameter</i>	<i>levels</i>
extraction temperature	30, 36, 45, 54 a 60°C
extraction time	45, 51, 60, 69 a 75 min
amount of NaCl	0,06, 0,125, 0,195 a 0,238 g

3 Results and discussion

A mixture of nitro aromatic compounds was used to determine the appropriate fibre for SPME extraction. Three types of fibres were tested (50/30 μm DVB/CAR/PDMS, 65 μm PDMS/DVB and 100 μm PDMS). The conditions for the extraction were as follows: temperature 50°C and time of extraction 20 min. Concentration of standards (2,4-DNT, NB, 4-NA, 4-NF a NN) was 10 mg/l.

Peak area was decisive for the choice of fibre. The results are presented in Figure 1. The 65 μm PDMS/DVB fibre was selected based on these results because the area of each compound is the best for this fibre.

The SPME extraction conditions were optimized for this fibre. The test parameters are shown in Table 1. A face-centred central composite design was used to optimise the response of the target components to a maximum. Optimal conditions for each compound are given in Table 2.

The optimum temperature 30°C for nitrobenzene was too low. Therefore, measurements were tested at this temperature and at 60 °C for NB. The results of this measurement are shown in Figure 2. These results indicate that the temperature of 30 °C is not sufficient. At a temperature of 60 °C is achieved a higher response at all concentration levels of nitrobenzene. For this reason, it has been proposed as optimal extraction conditions the following parameters: 75 min extraction time, extraction temperature 60 °C on fibre 65 μm PDMS/DVB. Calibration curves

were measured under these conditions of extraction. 100 μl was added to empty 22 mL screw-top vial. Standard solutions of the 2,4 - dinitrotoluene concentrations 1, 10, 25, 50 a 100 mg/l were used to construct calibration curve. Two types of swabs for collecting residues were tested. It was a swab of glass fibres and polypropylene (PP) fibres. Recoveries of these swabs were compared with the measurement solution in the empty vial. 100 μl of the standard solution was dispensed into an empty vial or swab of the test material. Swabs were placed into screw-top vials. The obtained calibration curves are shown in Figure 3. From these results it is seen that the peak area of the tampons are lower than the empty vial. Swab from glass fiber is more suitable for the collection of residue after the explosion. Low sensitivity would be obtained by using PP swab.

Table 2: Optimum conditions for SPME determination of nitro aromatic compounds

compound	extraction time [min]	extraction temperature [$^{\circ}\text{C}$]	amount NaCl [g]
NB	75	30	0,0595
2,4-DNT	75	60	0,238
4-NF	75	60	0,119
4-NA	75	37,5	0,238
NN	75	60	0,119

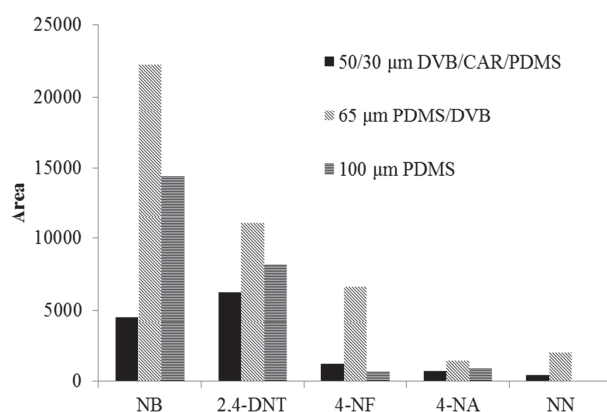


Figure 1: Dependence area on the fibres

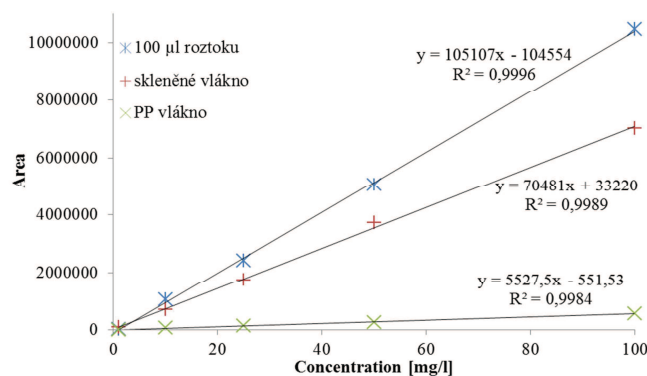


Figure 2: Calibration curve of the 2,4 - dinitrotoluene extracted from different materials.

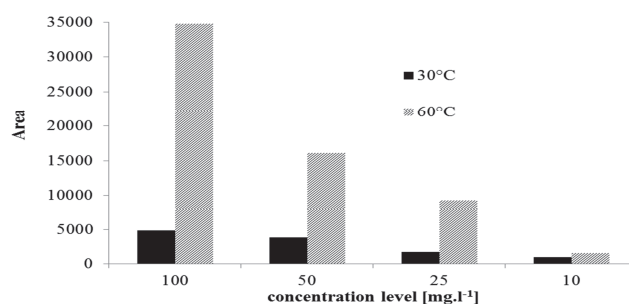


Figure 3: Effect of temperature on the extraction area at different concentrations of nitrobenzene.

4 Conclusion

The HS-SPME coupled with GC-MS is a rapid, simple, sensitive and solventless method. The use of a CCD in combination with SPME GC-MS analysis was successfully used to develop statistically valid optimised protocols for the selecting extraction conditions. In this work, suitable conditions for the determination of nitro aromatic compounds were searched. Results presented in this work show that this analytical method is sensitivity for their determination. Nitro aromatic compounds have been extracted using a 65 μm PDMS/DVB fibre that has shown the best efficiency for the extraction of those compounds. The optimal conditions have been extraction temperature 60 °C and extraction time 75 min. Glass fibre swab is better than a PP swab for the collection of residues.

Acknowledgments

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References

- [1] E.C. Bender, A.D. Beveridge, Investigation of pipe bombs, *Forensic Investigation of Explosions*, p. 429–492, **2011**
- [2] G. Sauzier, D. Bors, J. Ash, J.V. Goodpaster, S.W. Lewis, Optimisation of recovery protocols for double-base smokeless powder residues analysed by total vaporisation (TV) SPME/GC-MS, *Talanta* 158, p. 368–374, **2016**
- [3] D.A. DeTata, P.A. Collins, A.J. McKinley, A comparison of common swabbing materials for the recovery of organic and inorganic explosive residues, *J. Forensic Sci.* 58(3), p. 757–763, **2013**
- [4] D. Perret, et al., LC–MS–MS determination of stabilizers and explosives residues in hand-swabs, *Chromatographia*, 68 (7–8), p. 517–524, **2008**
- [5] J.D. Twibell, Assessment of solvents for the recovery of nitroglycerine from hands using cotton swabs, *J. Forensic Sci.*, 27 (4), p. 792–800, **1982**
- [6] D.A. DeTata, P.A. Collins, A.J. McKinley, A comparison of solvent extract cleanup procedures in the analysis of organic explosives, *J. Forensic Sci.*, 58(2), p. 500–507, **2013**
- [7] N. Song-im, S. Benson, C. Lennard, Evaluation of different sampling media for their potential use as a combined swab for the collection of both organic and inorganic explosive residues, *Forensic Sci. Int.*, 222(1–3), p. 102–110, **2012**

- [8] K. Szomborg, et al., Residues from low-order energetic materials: The comparative performance of a range of sampling approaches prior to analysis by ion chromatography, *Forensic Sci. Int.*, 233(1–3), p. 55–62, **2013**
- [9] N. Song-im, S. Benson, C. Lennard, Stability of explosive residues in methanol/ water extracts, on alcohol wipes and on a glass surface, *Forensic Sci. Int.*, 226 (1–3), p. 244–253, **2013**
- [10] P. Kolla, Stability of explosives traces on different supports, *Forensic Sci. Int.*, 60 p. 127–137, **1993**