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Influence of solvents and gas chromatographic injector conditions on the detectability of nitroaromatic compounds

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Abstract

We investigated the influence of four common solvents and of several liner packings of a split/splitless injector on the gas chromatographic behavior of trinitrotoluenes and related nitroaromatic compounds. The highest peaks are observed using toluene in combination with an empty liner or with a prepacked CarboFrit liner. In particular, the peaks of trinitrotoluene isomers and 1,3,5-trinitrobenzene significantly decreased or even totally disappeared when using quartz wool or glass wool, even when treated with dimethylchlorosilane. Similiar peak reductions are obtained with methanol or acetonitrile. Effects of decreasing peak are accompanied by the formation of two additional products when using methanol.

Keywords: Explosives; Injection methods; Instrumentation; Nitroaromatic compounds

1. Introduction

For decades soil and water contamination with explosives and related nitroaromatic compounds occurred in many military facilities and former ammunition plants as a consequence of waste disposal, burning, detonation, and demilitarization. 2,4,6-Trinitrotoluene (2,4,6-TNT) is the most common nitroaromatic contaminant. It is often accompanied by co-contaminants, such as dinitrotoluenes, aminodinitrotoluenes, and 1,3,5-trinitrobenzene [1,2]. Toluene, methanol, acetonitrile, and diethyl ether are solvents frequently used for the extraction of nitroaromatic compounds (NACs), where the choice of the solvent not only depends on the matrix of the environmental sample but also on the applied extraction methods [3–5].

Existing separation and detection techniques include spectroscopy, mass spectrometry, high-performance liquid chromatography (HPLC), gas chromatography (GC) and immunosensors. In addition to HPLC specifically, GC in combination with electron-capture detection (ECD) represents an important method for the analysis of trace amounts of NACs in environmental samples due to high sensitivity of ECD for these compounds.

In trace analysis the fast injection method is

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commonly applied to introduce diluted mixtures into split/splitless GC injectors. In contrast to the thermospray effect, which involves partial evaporation of the sample liquid inside the needle and nebulisation at the needle exit, solvent evaporation in the syringe needle is suppressed when using the fast injection method due to the short residence time. The solution leaving the needle forms a band of liquid, which passes through the vaporizing chamber at high velocity [6–11]. In the splitless mode the band of liquid is usually rejected and mostly falls back to the bottom where it forms a ball rotating at high speed [11]. To prevent the liquid passing through the insert and to achieve homogeneity of the sample, several types of vaporizing tubes have been tested and have proved to be more or less effective [11,12]. Schomburg et al. [13] obtained good results with a long and tight glass wool plug during split injection. According to Grob and co-workers [11,12] small amounts of packing material are sufficient to change the evaporation process completely. The density of the glass wool packing is not critical, provided that there are no large gaps between the glass fibers.

However, it is difficult to thoroughly deactivate packing material such as glass wool and quartz wool. Hence, these materials still exhibit active surface sites, which may give rise to adsorption, decomposition, conversion or other negative effects on sensitive sample components. For that reason, we investigated the influence of different liner packings on the gas chromatographic behavior of NACs. Furthermore, peak-reducing effects of several solvents on the detectability of NACs are described. To exclude any influence of a column on peak height all injections were split onto two different columns for separation of the NACs during GC analysis. Hence, the results obtained with one column can be confirmed by another column.

2. Experimental

2.1. Chemicals

Recrystallized trinitrotoluene isomers (2,3,4-TNT, 2,4,5-TNT, 2,4,6-TNT), aminodinitrotoluenes (2A-4,6DNT, 4A-2,6DNT), and 1,3,5-trinitrobenzene (TNB) were supplied by the Defence Institute for Materials, Explosives, Fuels and Lubricants (Swisttal, Germany). The nitrotoluenes (2-NT, 3-NT, 4-NT), 2,4-dinitrotoluene (2,4-DNT) and 1,3-dinitrobenzene (1,3-DNB) were purchased from Merck (Darmstadt, Germany). 2,6-dinitrotoluene (2,6-DNT) and 1,4-dinitrobenzene (1,4-DNB) were purchased from Riedel-de Haën (Seelze, Germany).

The stock solution was prepared with toluene. Prior to analysis the working standards were prepared by diluting the stock solution in toluene, methanol, methyl *tert*.-butyl ether (MTBE) and acetonitrile (ACN), respectively. The dilution factors were 1:1000 and 1:2000 for every solvent, thus obtaining final concentrations of 1.1–3.0 mg/l (1:1000) and 0.55–1.5 mg/l (1:2000) for the working standards.

2.2. Gas chromatography

NACs were analyzed using a Hewlett-Packard GC 5890 system equipped with a 7673A automatic sampler and two ECD systems. Hydrogen was used as carrier gas. Sample introduction (2 μl) was performed using the standard split/splitless type injector operated in the splitless mode. Splitless time was 30 s. After injection the sample was carried onto a retention gap (2 m×0.32 mm I.D., precolumn, uncoated, deactivated) followed by splitting onto two columns by means of a fused-silica y-connector. The first column was a MDN-12 column (60 m×0.25 mm I.D., Supelco) and the second was a XTI-5 column (57 m×0.25 mm I.D., Restek), both with a film thickness of 0.25 μm. The following temperature program was used: 1 min at 60°C, 60 to 120°C with 20°C/min, then 120 to 250°C with 3°C/min, followed by 10 min at 250°C. The injector and detector temperatures were 240°C and 300°C, respectively.

In addition to an empty splitless inlet liner (78.5 mm×4 mm I.D.×6.5 mm O.D., deactivated, single-taper at the bottom, Supelco) the following liner packings were tested: (a) quartz wool (Chrompack), (b) glass wool treated with dimethylchlorosilane (DMCS) (Chrompack), and (c) an inlet liner prepacked with a CarboFrit (Restek). The packing materials (22 mg quartz wool and 18 mg glass wool, respectively) were placed as small plugs in the

middle of identical liners, just below the end of the syringe needle.

2.3. Mass spectrometry (MS)

Mass spectra were obtained using a Hewlett-Packard HP 6890 system with a MSD 5973 and an automatic sampler 7683. NACs were determined using electron impact ionization (EI) conditions and the scan mode. Separations were performed on a HP-5 MS column (30 m×0.25 mm I.D., 0.25 μm film thickness, Hewlett-Packard).

3. Results

A good separation is obtained for all NACs when using the XTI-5 column. On the MDN-12 column (confirmation column) a change in elution sequence is observed; separation for 2,3,4-TNT, 2,4,5-TNT, and TNB is poor but sufficient. Table 1 shows the corresponding retention times, heights and sensitivities of the NACs for both columns (MDN-12 and XTI-5) in combination with an empty injector liner. The heights listed in Table 1 are mean values calculated from five measurements using the 1:1000 toluene dilution, corresponding to concentrations of 1.1–3.0 mg/l for every compound. The relative standard deviations of the compounds are smaller than 4% for both dilutions (1:1000 and 1:2000) and for both columns. Since the MDN-12 column was fresher it probably contained less active sites than the older XTI-5 column. Hence, the NACs show narrower and higher peaks when using the MDN-12 column. In addition, two different ECD systems were used: the MDN-12 column was connected to an ECD with an anode purge, and the XTI-5 column was connected to an older type without anode purge. Upon comparing both columns this leads to varying heights and thus to varying sensitivities. These are calculated as ratio of the peak height to the amount of the respective compound.

3.1. Effects of liner packing material

Identical liners packed with quartz wool, DMCS-treated glass wool and an inlet liner prepacked with CarboFrit were used in order to test the influence of the packing material on the chromatographic behavior of the NACs.

For every packing material representative chromatograms obtained with the XTI-5 column are displayed in Fig. 1 together with a chromatogram obtained with an empty liner (top of figure). Overall, the chromatogram obtained with the CarboFrit liner resembles the chromatogram obtained with the empty liner. In contrast, both the DMCS material and the quartz wool lead to significantly reduced peak

Table 1
Retention times (t_R), heights, and sensitivities of nitroaromatic compounds (1:1000 dilution in toluene) and using columns MDN-12 and XTI-5 ($n=5$)

Substance	No.	MDN-12			XTI-5		
		t_R (min)	Height (μV)	Sensitivity (μV/pg)	t_R (min)	Height (μV)	Sensitivity (μV/pg)
2-NT	1	11.974	7467	3.2	9.828	6212	2.7
3-NT	2	13.251	9254	4.0	10.630	9607	4.2
4-NT	3	13.936	4841	2.0	11.034	5211	2.2
2,4-DNT	4	26.879	109765	51	20.636	59765	28
2,6-DNT	5	22.868	121364	112	18.116	73061	68
2,3,4-TNT	6	37.623	127832	108	31.193	75204	64
2,4,5-TNT	7	37.749	183583	60	29.986	97822	32
2,4,6-TNT	8	35.337	111752	108	26.667	65844	64
2A-4,6DNT	9	43.660	107334	55	36.677	58988	30
4A-2,6DNT	10	41.166	121430	58	34.870	67656	32
1,3-DNB	11	23.598	63111	27	17.773	34567	15
1,4-DNB	12	23.239	120986	111	17.064	63531	58
TNB	13	37.461	97431	47	26.201	50193	24

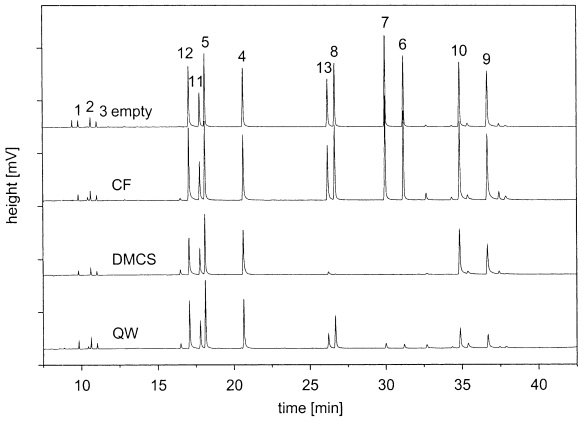

Fig. 1. Chromatograms of nitroaromatic compounds diluted in toluene using an empty liner, a liner prepacked with CarboFrit (CF), DMCS glass wool (DMCS), and quartz wool (QW) as packing material. (For peak numbering, see Table 1).

heights of several NACs. To quantify these effects relative heights were calculated as ratios of the heights of the NACs obtained with the respective packing material to the heights obtained with the empty liner. The heights used for calculation are mean values of five measurements for every packing material and for both dilutions (1:1000 and 1:2000).

The strongest effects are observed especially with the three TNT isomers and TNB. For both columns relative heights of 0 to 3% are obtained with DMCS glass wool, suggesting that DMCS glass wool completely decomposes or adsorbs these compounds. When using quartz wool the same applies true for 2,3,4-TNT and 2,4,5-TNT, whereas 2,4,6-TNT and TNB yield relative heights of about 39 and 20%, respectively. Poor recoveries are also observed for 2A-4,6DNT and 4A-2,6DNT, especially when using quartz wool; in this case the relative heights ranged from 17 to 25%. With the exception of 1,4-DNB and DMCS glass wool, a weaker influence is observed for dinitrotoluenes and dinitrobenzenes, with relative heights exceeding 61%. In contrast, the prepacked CarboFrit material has no significant effect on the chromatographic behavior of the NACs. Rather, recoveries up to 118% may indicate a slight increase in heights relative to an empty liner.

Similar peak height decreases are observed in both columns, indicating that decomposition or adsorption of NACs take place in the injector system. The contact surface in the liners increase when using quartz wool or DMCS glass wool. The larger the contact surface the greater the number of active sites enhancing adsorption, degradation or other negative effects.

3.2. Solvent effect

Several solvents are used for the extraction of NACs from environmental matrices. Methanol and acetonitrile are frequently used in combination with sonification. MTBE is selected to represent ethers which are used in combination with Soxhlet extraction. Due to the excellent gas chromatographic properties of toluene and its chemical similarity to the NACs, peak heights obtained with toluene serve as reference values. Five measurements were performed with every solvent and both dilutions (1:1000 and 1:2000) using an empty liner. For the XTI-5 column representative chromatograms are displayed in Fig. 2.

All three solvents significantly affect the chromatographic behavior of the TNT isomers. Using methanol their heights decrease by more than 78%, and a total peak disappearance is even noted with acetonitrile. Likewise, poor recoveries of 23 to 33% are found with 2,3,4-TNT and 2,4,5-TNT, when MTBE is used, whereas a lesser influence is observed with 2,4,6-TNT, with recoveries ranging from

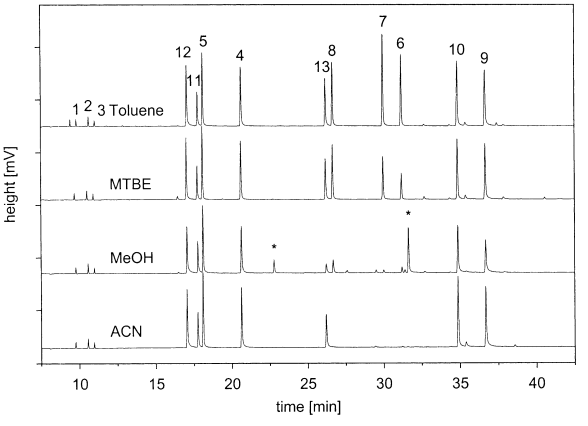

Fig. 2. Chromatograms of nitroaromatic compounds diluted in toluene, methyl tert.-butyl ether (MTBE), methanol (MeOH), and acetonitrile (ACN), using an empty liner (* transformation products).

69% (MDN-12) to 75% (XTI-5). Furthermore, the peak height of TNB strongly depends on the solvents used for the standard solutions. The lowest relative height is observed with methanol (20%), followed by acetonitrile (51%) and MTBE (70%). In contrast to the TNT isomers and TNB, acetonitrile does not significantly influence the peak heights of mononitrotoluenes, dinitrotoluenes, aminodinitrotoluenes, and dinitrobenzenes, compared to toluene. Using MTBE, peak heights of these compounds decrease by up to 20%, whereas peaks decrease by up to approximately 50% when methanol is used.

Two additional transformation products are observed when using methanol. They show retention times of 22.8 and 31.6 min with the XDI-5 column and of 27.9 and 38.3 min with the MDN-12 column. The formation of these compounds suggests that methanol usage not only contributes to the decomposition of the NACs, but also takes part in the chemical reactions occuring in the inlet.

To elucidate the structure of the compounds mass spectrometry was applied to the methanol standard mixture. The same effects on peak heights are observed with GC–MS. However, the peak at 22.8 min (XTI-5) is too low to obtain good mass spectra. Fig. 3 shows the mass spectrum corresponding to the peak at 31.6 min (XTI-5).

When a nitro substituent is in the ortho position with respect to a methyl group the mass spectrum is modified in two ways: (a) The intensity of the molecular ion [M] is substantially reduced, and (b) the initial fragmentation is dominated by loss of a hydroxyl radical [M-17] [14]. Assuming that the mass of 212 represents the molecular ion, the loss of a hydroxyl radical leads to the base peak at 195. In addition, the mass of the molecular ion is an even number, indicating the presence of only two nitrogen atoms. Hence, one of the three TNT nitro groups may be substituted during a reaction. For NACs, secondary fragmentation of the [M-17] ions primarily occurs through loss of either NO or NO_2. Loss of one NO corresponds to mass 165. Further fragmentation of the 165 ion yields mass 135 due to the loss of a second NO, whereas loss of NO_2 yields mass 119. Subsequent ion 165 fragmentation may also occur either through loss of a second hydroxyl radical, resulting in mass 148 or through loss of CH_3OH, resulting in mass 133, which shows nearly the same height as mass 135. Overall, the 212 molecular ion along with the fragmentation pattern may correspond to the formula $C_8H_8N_2O_5$ and to the formation of a dinitromethoxytoluene. Due to the high injector temperature (240°C) and the excessive presence of methanol, TNT may undergo methoxylation along with the elimination of a nitro group. However, further investigation is necessary to identify the compounds formed during injection.

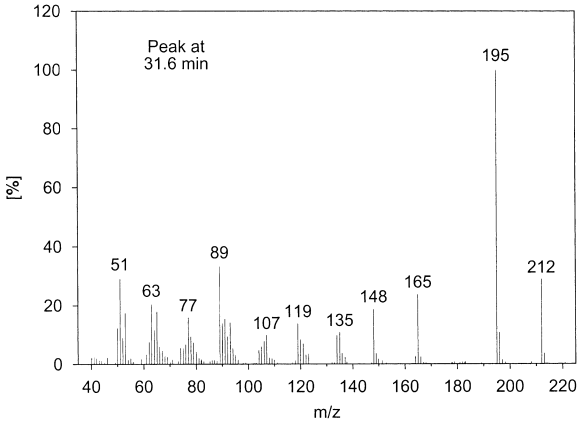

Fig. 3. Mass spectrum of the unknown peak eluting at 31.6 min with the XTI-5 column.

4. Conclusions

Our findings demonstrate that the packing material of the liner strongly influences the detectability of NACs, especially of TNT isomers and TNB. These compounds are known to be sensitive to bases, and hence may be suited for testing interactions to bases in gas chromatographic systems [15]. In addition, the solvent used for injection significantly affects detectability and sensitivities of TNT isomers and TNB. Among the solvents tested toluene proved to be the most appropriate chemical, whereas methanol and acetonitrile contribute to the decomposition and transformation of TNT isomers and TNB. Optimization of injection conditions and rigorous attention to system activity are essential to accurate and reproducible chromatographic analysis of trace amounts of NAC.

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