



Research paper / Praca doświadczalna

Comparing the application of GC/FID and GC/MS methods in the quantitative analysis of 3-nitrotoluene in an excess of 2- and 4-nitrotoluene in products of toluene nitration *Porównanie zastosowania metod GC/FID oraz GC/MS w oznaczaniu zawartości 3-nitrotoluenu w produktach nitrowania toluenu wobec nadmiaru 2- i 4-nitrotoluenu*

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Abstract: Comparison of gas chromatographic methods GC/FID and GC/MS for quantification of 3-nitrotoluene (3-NT) in the presence of high concentrations of 2-nitrotoluene and 4-nitrotoluene, is presented. GC/FID linear regression allows calibration curves in the concentration range of mononitrotoluene (MNT) 0.5-10 mg/ml to be obtained. For GC/MS, a non-linear dependence of detector signal was observed, particular for higher MNTs concentrations. However, calibration data could be fitted stepwise with three separate calibration lines. Using regression parameters, detection and quantification limits of GC/FID and GC/MS methods were determined. Their values proved to be comparable for both methods. The experiments showed that determination of small concentrations of 3-NT in a large excess of the others is possible using both calibration curves and peak area i.e. in percentage terms.

Streszczenie: Opracowano procedurę ilościowego oznaczania mononitrotoluenów (MNTs) wykorzystując metodę GC/FID oraz GC/MS. Dla GC/FID uzyskano krzywe kalibracyjne w zakresie stężeń MNT 0,5-10 mg/ml. Dla GC/MS nie dopasowano wszystkich punktów kalibracyjnych metodą regresji liniowej. Dane te dopasowano metodą regresji nieliniowej. Dla uproszczenia oznaczeń ilościowych dane dla GC/MS dopasowano metodą regresji liniowej przy pomocy trzech krzywych kalibracyjnych. Wykorzystując parametry regresyjne wyznaczono granice wykrywalności i granice oznaczalności obu metod. Wartości tych granic, po uwzględnieniu niepewności pomiarowych, uznano za jednakowe. Badania wykazały, że oznaczanie niewielkich zawartości 3-NT w obecności nadmiaru pozostałych MNTs, wymaga odpowiedniego doboru stężeń próbek. Wtedy 3-NT można oznaczyć przy pomocy krzywych kalibracyjnych, jak i na podstawie procentowego udziału pól powierzchni pików MNT.

Keywords: nitrotoluenes, GC/FID method, GC/MS method, quantitative analysis, limits of detection, limits of quantification

Słowa kluczowe: nitrotolueny, metoda GC/FID, metoda GC/MS, analiza ilościowa, granica wykrywalności, granica oznaczalności

Symbols and abbreviations

| | |
|--------|--|
| 2-NT | 2-Nitrotoluene |
| 3-NT | 3-Nitrotoluene |
| 4-NT | 4-Nitrotoluene |
| FID | Flame Ionization Detector |
| GC/FID | Gas Chromatography with Flame-Ionization Detection |
| GC/MS | Gas Chromatography with Mass Spectrometry |
| IS | Internal standard |
| LOD | Limit of Detection |
| LOQ | Limit of Quantification |
| MNT(s) | Mononitrotoluene(s) |
| MS | Mass Spectrometer |
| PNA | <i>p</i> -Nitroaniline |
| TLC | Thin-Layer Chromatography |

1. Foreword

For many decades, 2,4,6-trinitrotoluene (TNT), has been the most commonly used military explosive. Although TNT can be obtained using many synthesis techniques [1], a characteristic and disadvantageous effect of its production processes is that, apart from the main products, i.e. 2- and 4-nitrotoluene (2-NT and 4-NT, respectively), a small amount of 3-nitrotoluene (3-NT) is formed in the first nitration stage. 3-NT formed in this synthesis stage is particularly undesirable, since, as a result of further nitration of the MNT mixture, unsymmetrical trinitrotoluenes are formed. The presence of unsymmetrical trinitrotoluenes in TNT significantly reduces its melting point and stability [2]. A bisulfite washing is used to remove the unsymmetrical trinitrotoluenes from TNT. However, the process is very harmful to the environment. A large amount of effluent i.e. red water is collected in the sedimentation tanks. The process of removing the toxic nitroaromatic compounds from the effluent or sediments is very complex [1].

GC is one of the methods used to analyse nitroaromatic compounds and results from their properties, i.e. solubility in volatile solvents, low melting points, thermal stability and lack of strong polar functional groups, including $-OH$ and $-NH_2$. The main and practically only issue related with instrumentation when using gas chromatography in their analysis is the choice of a suitable detector and chromatographic column. A flame ionization detector (FID) is most commonly used in gas chromatography, however, it shows lower sensitivity to explosives than other detectors, namely, an electron capture detector (ECD), a nitrogen-phosphorus detector (NPD) or a flame photometric detector (FPD). None of these provides as much information on the molecular structure as a mass spectrometry detector (MS). A short review of literature in which those detectors were used is presented below. An example of the use of the GC/FID method available in literature is the analysis of nitroaromatic compounds in sewage from the production and treatment of raw TNT [3] and the analysis of liquid laboratory waste [4]. A dispersive liquid-liquid microextraction – a method allowing a 200 to 300-fold enrichment of explosives – was used. Slovakian researchers presented a GC/MS method using a maximum sample injection with complete evaporation of the solvent (PTV) which was also compared with GC/ECD for analysis of simulated samples of explosives [5]. The PTV method allows injection of substance amounts up to 1,000-times greater per column compared to ‘conventional’ injections. The Hewitt and Jenkins study [6] is an example of using a NPD detector. A portable gas chromatograph was used in the study and the analyses were carried out in the field. Table 1 shows the literature data including the limits of detection and quantification of selected explosives given in the referenced literature [4, 5].

Table 1. Limits of detection (LOD) and quantification (LOQ) of explosives for GC/MS, GC/ECD and GC/FID methods quoted in literature

| Substance | LOD [ng/ml] | | | LOQ [ng/ml] | | |
|--------------------|-------------------|--------|---------------------|-------------|--------|--------|
| | GC/MS | GC/ECD | GC/FID | GC/MS | GC/ECD | GC/FID |
| Nitrobenzene | 0.071 | 0.32 | – | 0.24 | 1.10 | – |
| 2-NT | 0.280 | 0.22 | 0.090 | 0.95 | 0.72 | 0.27 |
| 3-NT | 0.170 | 0.55 | 0.106 | 0.57 | 1.80 | 0.32 |
| 4-NT | 0.065 | 1.10 | 0.094 | 0.22 | 3.60 | 0.28 |
| 2,6-DNT | 0.088 | 0.18 | 0.40 | 0.29 | 0.61 | 1.20 |
| 2,4-DNT | 0.063 | 0.41 | 0.50 | 0.21 | 1.40 | 1.50 |
| TNT | 0.029 | 0.41 | 0.09 | 0.096 | 1.40 | 0.27 |
| PETN ^{a)} | 0.130 | 33 | – | 0.44 | 110 | – |
| RDX ^{b)} | 27 | 0.60 | – | 89 | 2 | – |
| Enrichment method | PTV ^{c)} | | DLLME ^{d)} | PTV | | DLLME |
| Literature | [5] | | [4] | [5] | | [4] |

Notes:

^{a)} PETN – pentaerythritol tetranitrate, pentrite; ^{b)} RDX – 1,3,5-trinitro-1,3,5-triazinane, hexogen; ^{c)} PTV – a method combining maximum sample injection volume with complete solvent evaporation; ^{d)} DLLME is an abbreviation for a dispersive liquid-liquid microextraction method

The study aimed to develop a method for the quantitative analysis of MNTs using gas chromatography with FID and MS detection. It aimed to use this to analyse the MNT samples containing small amounts of 3-NT against the significantly higher 2-NT and 4-NT content. It relates to the issue, discussed above, of the formation of unsymmetrical derivatives of TNT [1]. The calibration curves for quantitative analyses will be prepared using a linear regression method and an internal standard (IS) method. The limits of detection and quantification will be determined based on the regression data. Using the control samples, a capability of determining small amounts of 3-NT in the samples containing a 2 to 20-fold and 10 to 100-fold excess of 2-NT and 4-NT, will be verified. A capability of determining the MNT content in samples based on a percentage share of MNT area in the chromatograms, will also be verified. The latter, if consistent with data based on the calibration curves, will significantly facilitate the quantitative analysis of the MNT and will eliminate time-consuming and costly calibrations.

2. Experimental section

2.1. Materials

Solutions of MNTs (2-NT, 3-NT and 4-NT) in acetonitrile at concentrations ranging from 0.1 to 10 mg/ml, were prepared. The IS solution – *p*-nitroaniline (PNA), at a concentration of 40 mg/ml, was prepared using the same solvent. The solutions were prepared using HPLC grade acetonitrile; 2-NT, 3-NT and 4-NT, and PNA were obtained from Sigma-Aldrich. The following measuring glassware was used: 5, 10, 25 and 50 ml flasks; 0.2 to 10 ml automatic measuring pipettes and an analytical balance.

2.2. Test methods

2.2.1. Test equipment

A gas chromatograph with flame ionization detector (GC-FID) by PERKIN ELMER (Autosystem XL) and an Agilent 7890A gas chromatograph coupled with Agilent Technologies 5975C VL MSD mass selective detector, were used.

2.2.2. GC/FID method

- injection: 2 μl , gas stream distribution: 1:50,
- dispenser temperature: 250 $^{\circ}\text{C}$,
- temperature program: 70 $^{\circ}\text{C}$ for 1 min, increased by 25 $^{\circ}\text{C}/\text{min}$ up to 250 $^{\circ}\text{C}$, maintained for 11.8 min, analysis time – 20 min,
- carrier gas: nitrogen 1 ml/min,
- Perkin Elmer Elite – 1701 column (length 30 m, inner diameter 0.53 mm, film thickness 1 μm).

2.2.3. GC/MS method

- injection: 0.1 μl , gas stream distribution: 1:250,
- dispenser temperature: 250 $^{\circ}\text{C}$,
- temperature program: 40 $^{\circ}\text{C}$ for 2 min, increased by 5 $^{\circ}\text{C}/\text{min}$ up to 70 $^{\circ}\text{C}$, increased by 25 $^{\circ}\text{C}/\text{min}$ up to 250 $^{\circ}\text{C}$, maintained for 14.8 min, analysis time 30 min,
- carrier gas: helium 1 ml/min,
- Agilent HP-1701 14% Cyanopropyl Phenyl column (length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm).

2.2.4. Choosing the IS

The IS method involves adding a fixed amount of component (standard) to each sample, where, that component is not present in the sample. The requirements for the IS are available from many sources, e.g. Encyclopaedia of Chromatography [7]. A calibration curve is prepared based on the analysis of standard samples, at different concentrations, containing the IS. Based on several measurements (e.g. 3 to 5), the average ratios between the areas of the peaks of determined substances and the standard are determined, and a linear regression method is used to determine the relationship between those values and the concentration of the determined substance. In the case of the determined samples, the same amount of standard is added and, based on the area ratio, their concentration is determined.

2.2.5. Determining the limits of detection (LOD) and quantification (LOQ)

Based on the parameters of the determined calibration curves, i.e. the slope of the calibration curve – a , the residual standard deviation – s_{xy} (method I) and the standard deviation of the absolute term of the curve – s_b (method II), the limits of detection and quantification [8] of MNTs were determined. The following two equations were used:

$$LOD = \frac{3.3 s}{a} \quad (1)$$

$$LOQ = 3LOD \quad (2)$$

where a is the slope of the calibration curve and s is a standard deviation (s_{xy} or s_b).

3. Results and discussion

3.1. Choosing the IS

Based on a preliminary analysis, three nitroaromatic compounds which met the requirements for the IS were selected [7]: PNA, 1-nitronaphthalene and 1,8-dinitronaphthalene. The analysed MNTs eluted between 8 to 9 min (GC/FID) and 12 to 13 min (GC/MS). PNA, which in both methods eluted in approx. 15 min, was used as the IS in further studies. PNA was characterised by good separation from

the MNT, yielding the most symmetrical peak and the highest signal in TIC (total ion current) mode in the GC/MS analysis. Figures 1 and 2 show the chromatograms.

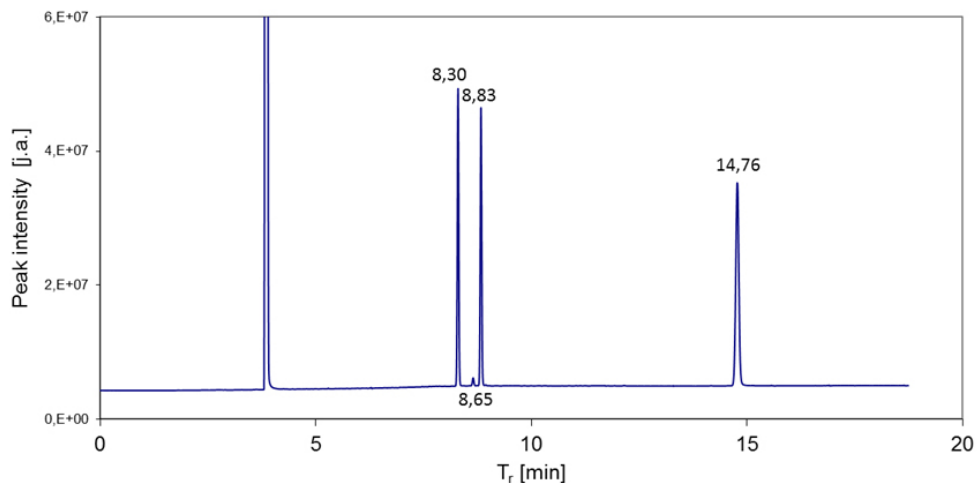


Figure 1. GC/FID chromatogram for MNTs and the IS: 2-NT (8.30 min), 3-NT (8.65 min), 4-NT (8.63 min), PNA (14.76 min)

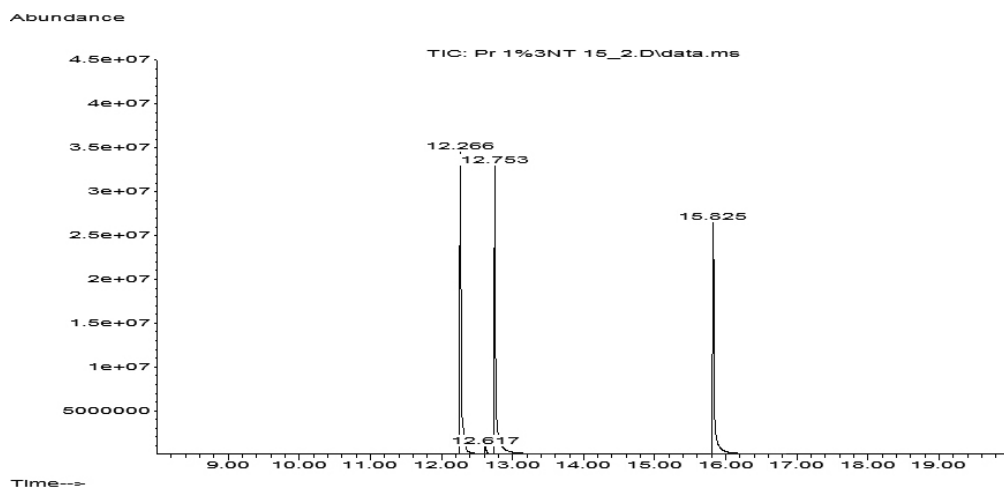


Figure 2. GC/MS chromatogram for MNTs and the IS: 2-NT (12.26 min), 3-NT (12.61 min), 4-NT (12.75 min), and PNA (15.82 min)

3.2. Calibration curves

The calibration curves obtained using the IS are shown in Figure 3 (GC/FID) and Figure 4 (GC/MS). For the FID detector, linear calibration curves were obtained within the concentration range from 0.5 to 10 mg/ml, with the parameters listed in Table 2. For the MS detector, no linear calibration curves were obtained within the concentration range of 0.1 to 10 mg/ml used in the analysis (Figure 4). The curves were obtained by fitting the experimental points with quartic polynomials at $R^2 = 0.999$. For the cubic polynomial, R^2 was 0.997 and for orders of polynomial over 4 this did not change, remaining at 0.999.

The non-linear regression observed in the qualitative analysis is not a rare occurrence for MS detectors and can be explained by the change in ionisation conditions in the presence of a large number of ions in the MS source, secondary reactions and fragmentation of molecules. Similar phenomena have been observed using the GC/MS method, e.g. in the analysis of barbiturates [9] or volatile organic compounds (VOCs), e.g. acetaldehyde and hexyl alcohol [10].

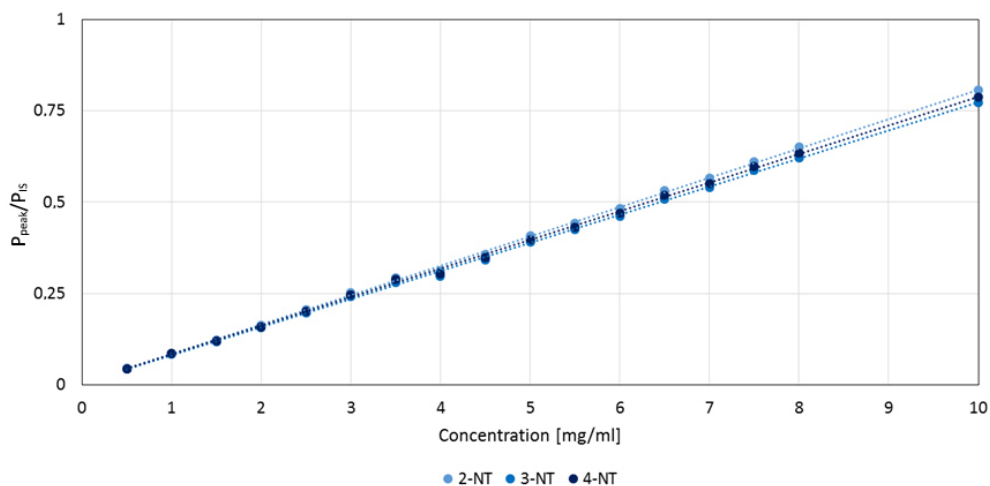


Figure 3. Calibration curves for the GC/FID method – IS method

The analysis of the GC/MS calibration curves (Figure 4) shows that there are concentration ranges characterised by a linear relationship between the MS detector signals. Starting with the lowest concentration, the highest concentration was determined for which the best linear regression fit parameters were obtained. The same procedure was carried out for higher concentrations. Starting with the highest concentration, determined from the fit for the range of lower concentration, the highest concentration with the best linear fit was determined. Three ranges of MNT concentration were determined for which correlation lines of the MS detector signal were observed. Table 2 shows the linear regression parameters for individual MNTs using the GC/MS method, and Figure 5 shows the calibration curves.

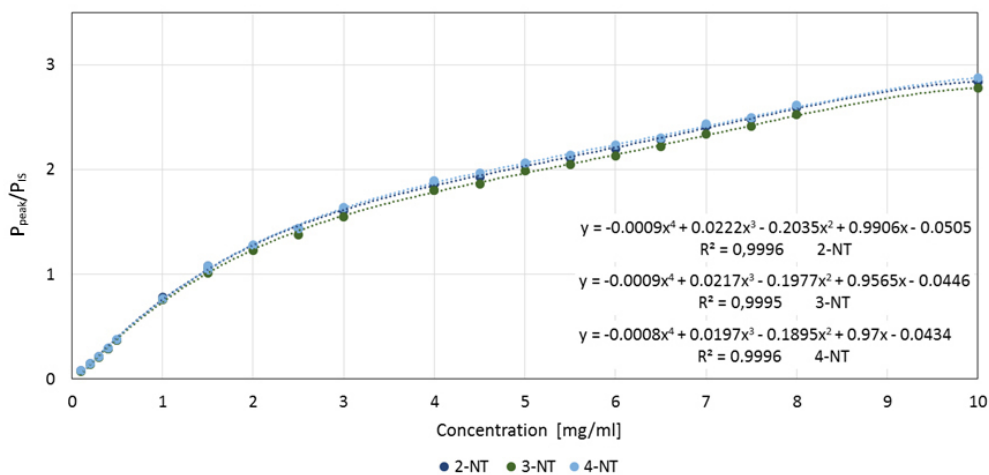


Figure 4. Calibration curves for the GC/MS method (IS method); calibration curves obtained using a non-linear regression method; calculated quartic polynomial equations are shown in the figure

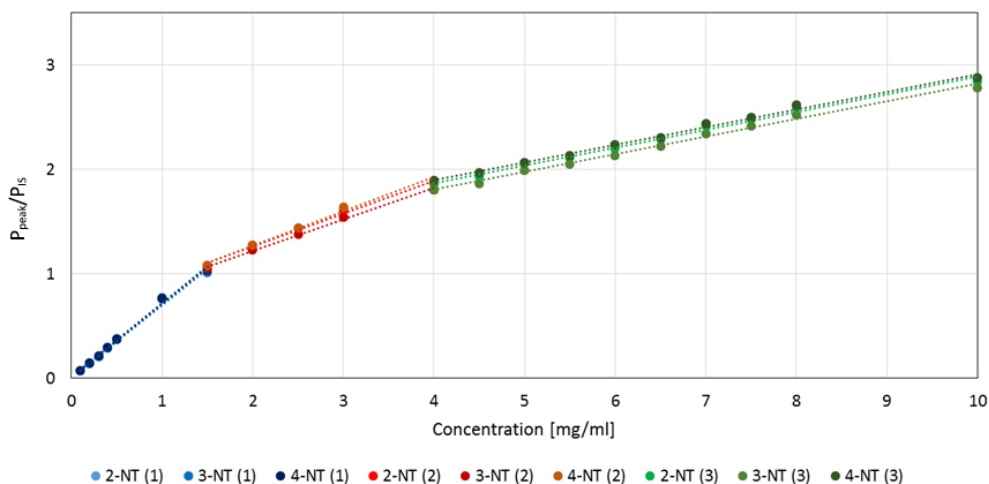


Figure 5. Calibration curves for the GC/MS method (IS method); the designations (1), (2) and (3) in the description of the MNT markers applying to the subsequent ranges of calibration solution concentrations: (1) 0.1-1.5 mg/ml, (2) 1.5-4 mg/ml, (3) 4-10 mg/ml

Table 2. Regression parameters of calibration curves for the analysed MNTs using GC/FID and GC/MS methods with the IS

| Compound | GC/FID Concentrations of MNT calibration samples from 0.5 to 10 mg/ml | | | | | |
|----------|---|----------|-----------|----------|----------|-------------|
| | $a^a)$ | $b^b)$ | $R^{2c)}$ | $s_a^d)$ | $s_b^e)$ | $s_{xy}^f)$ |
| 2-NT | 0.080326 | 0.003859 | 0.999 | 0.000527 | 0.002781 | 0.000494 |
| 3-NT | 0.076932 | 0.003873 | 0.999 | 0.000517 | 0.002729 | 0.000453 |
| 4-NT | 0.078353 | 0.004137 | 0.999 | 0.000529 | 0.002792 | 0.000525 |
| Compound | GC/MS concentrations of MNT calibration samples from 0.1 to 1.5 mg/ml | | | | | |
| | $a^a)$ | $b^b)$ | $R^{2c)}$ | $s_a^d)$ | $s_b^e)$ | $s_{xy}^f)$ |
| 2-NT | 0.712529 | 0.010021 | 0.995 | 0.024686 | 0.018188 | 0.004553 |
| 3-NT | 0.693047 | 0.011694 | 0.995 | 0.027227 | 0.02006 | 0.005577 |
| 4-NT | 0.704142 | 0.015745 | 0.995 | 0.022291 | 0.016424 | 0.003721 |
| Compound | GC/MS concentrations of MNT calibration samples from 1.5 to 4.0 mg/ml | | | | | |
| | $a^a)$ | $b^b)$ | $R^{2c)}$ | $s_a^d)$ | $s_b^e)$ | $s_{xy}^f)$ |
| 2-NT | 0.31290 | 0.638063 | 0.992 | 0.016996 | 0.046546 | 0.003167 |
| 3-NT | 0.300197 | 0.621736 | 0.992 | 0.0119 | 0.03259 | 0.001550 |
| 4-NT | 0.326798 | 0.616909 | 0.992 | 0.017259 | 0.047267 | 0.003309 |
| Compound | GC/MS concentrations of MNT calibration samples from 1.5 to 4.0 mg/ml | | | | | |
| | $a^a)$ | $b^b)$ | $R^{2c)}$ | $s_a^d)$ | $s_b^e)$ | $s_{xy}^f)$ |
| 2-NT | 0.169790 | 1.191985 | 0.995 | 0.005547 | 0.036752 | 0.007127 |
| 3-NT | 0.169075 | 1.130678 | 0.994 | 0.004827 | 0.031985 | 0.005544 |
| 4-NT | 0.169168 | 1.220586 | 0.995 | 0.004461 | 0.029557 | 0.004727 |

Notes:

^{a)} slope of the calibration curve; ^{b)} absolute term of the calibration curve; ^{c)} squared correlation coefficient; ^{d)} standard deviation of the slope; ^{e)} standard deviation of the absolute term; ^{f)} residual standard deviation of the calibration curve

The slopes of the MNT calibration curves for the GC/FID method are similar. For the GC/MS method, the slopes of the calibration curves within the range of the lowest concentrations are higher by an order of magnitude being approx. 0.70. It is worth noting that for two subsequent concentration ranges, the slopes are reduced twofold and are approx. 0.30 and 0.16. The slopes of the MNT calibration curves for the GC/MS method (see GC/FID) are very similar. The result, from the point of view of further quantitative determination, e.g. using the IS normalisation of the peak areas, is both positive and surprising. This stems from the fact that the MS fragmentation of 3-NT and 4-NT is similar – high-intensity molecular ions and 91 m/z tropylium ion) can be observed [11, 12], whereas, the fragmentation of 2-NT [13] follows the α -elimination (OH radical) path and 65 and 120 m/z ions are dominant. The intensity of the ions is different and thus, completely different ion currents and slopes can be expected. For the FID detector, the dominant parameter affecting signal intensity is the carbon content in the analyte particles which, in the case of MNT isomers, yields, as expected, similar slopes of the calibration curves. As a conclusion to this discussion it should be highlighted that the almost 10-fold differences in the calibration curve slopes are mainly due to differences in the methods of obtaining the FID and MS detector signals and the peak intensity units used in the software. At this stage, there is no point in discussing the differences in the detection capabilities of both detectors.

Based on Equations 1 and 2 and the regression data (Table 2), the limits of detection (LOD) and the limits of quantification (LOQ) for the MNTs analysed using two chromatographic systems, were determined. Table 3 shows the data. The LODs and LOQs calculated, based on the residual standard deviation of the calibration curve for the FID and MS detectors, are similar. For the FID detector, the LODs range from 0.019 to 0.022 mg/ml, and the LOQs – from 0.058 to 0.066 mg/ml. For the MS detector, the LODs range from 0.017 to 0.027 mg/ml, and the LOQs – 0.052 to 0.080 mg/ml.

The Student's t-test [8] ($\alpha = 0.05$, two independent tests, at different variances, two-sided test) for average

LOD and LOQ values was used for both methods. For LODs and LOQs calculated based on the residual standard deviation, the determined statistics (-0.92 and -0.39) are outside of the critical range (Student's t -test = 4.30) which means that both the average LOD and LOQ values are identical for both methods. For LODs and LOQs calculated based on the standard deviation of the absolute term, the determined statistics (5.40 and 5.55) are within the critical range (Student's t -test = 4.30) which means that both the average LOD and LOQ values are different for both methods.

Table 3. Limits of detection (LOD) and quantification (LOQ) of MNTs for GC/FID and GC/MS methods, determined using linear regression for the data obtained from the calibration using the IS

| Based on the residual standard deviation of the calibration curve | | | | | | | | | | | | |
|---|-------------|-------|-------|-------------|-------|-------|-------------|-------|-------|-------------|-------|-------|
| Calibration concentration range [mg/ml] | GC/FID | | | | | | GC/MS | | | | | |
| | LOD [mg/ml] | | | LOQ [mg/ml] | | | LOD [mg/ml] | | | LOQ [mg/ml] | | |
| | 2-NT | 3-NT | 4-NT | 2-NT | 3-NT | 4-NT | 2-NT | 3-NT | 4-NT | 2-NT | 3-NT | 4-NT |
| 0.5-10 | 0.020 | 0.019 | 0.022 | 0.061 | 0.058 | 0.066 | – | – | – | – | – | – |
| 0.1-1.5 ^c | – | – | – | – | – | – | 0.021 | 0.027 | 0.017 | 0.063 | 0.080 | 0.052 |
| Based on the standard deviation of the absolute term of the calibration curve | | | | | | | | | | | | |
| Concentration range [mg/ml] | GC/FID | | | | | | GC/MS | | | | | |
| | LOD | | | LOQ | | | LOD | | | LOQ | | |
| | 2-NT | 3-NT | 4-NT | 2-NT | 3-NT | 4-NT | 2-NT | 3-NT | 4-NT | 2-NT | 3-NT | 4-NT |
| 0.5-10 | 0.114 | 0.117 | 0.118 | 0.343 | 0.351 | 0.353 | – | – | – | – | – | – |
| 0.1-1.5 | – | – | – | – | – | – | 0.084 | 0.096 | 0.077 | 0.253 | 0.287 | 0.231 |

Since the correspondence of LOD and LOQ values has been shown for the GC/FID and GC/MS methods and calculated based on the residual standard deviation, the quantitative determination of MNT can be compared directly in different samples. Table 4 shows results obtained using the regression line discussed above, based on the percentage of MNT areas. Samples containing 2-NT and 4-NT at 1, 5 and 10 mg/ml and 3-NT at 0.1 and 0.5 mg/ml, were analysed. For easy comparison of results, values obtained using the IS method, expressed in mg/ml, were converted into a percentage of individual MNTs in the mixtures. Results in the form of percentage areas of individual MNTs were used as the percentage content of individual nitrotoluenes in the samples. For MNT samples containing 3-NT at 0.5 mg/ml, and other substances at 1 and 5 mg/ml, the IS method for the GC/FID and GC/MS analysis yields reliable results. In this case, the relative (percentage) error is less than 5%. For the same samples, the IS normalisation method (percentage of peak areas) yields a result similar to that observed for the GC/FID method. For this type of estimation of MNT content, the GC/MS method only yields the correct results for 2-NT and 4-NT at 1 mg/ml. For 2-NT and 4-NT at 10 mg/ml, determining the 3-NT content at 0.5 mg/ml introduces large errors ranging from 13% to 176%.

Table 4. Determining 3-NT content in mixtures with other MNTs; MNT concentrations 2 to 20 times higher than 0.5 mg/ml 3-NT and 10 to 100 times higher than 0.1 mg/ml 3-NT

| 0.5 mg/ml 3-NT content [wt.%) in the MNT mixture | | | | | | | | |
|--|--|--|-------|--|-----------------------------------|--|-------|--|
| Calculated amount | Based on calibration using the IS method | | | | Based on percentage MNT areas | | | |
| | GC/FID | Error ^{d)} (BW) ^{e)} | GC/MS | Error ^{d)} (BW) ^{e)} | GC/FID | Error ^{d)} (BW) ^{e)} | GC/MS | Error ^{d)} (BW) ^{e)} |
| 20.00 ^{a)} | 19.09 | -0.91 (4.5) | 20.46 | 0.46 (2.3) | 20.60 | 0.60 (3.0) | 19.31 | -0.69 (3.4) |
| 4.76 ^{b)} | 4.84 | 0.08 (1.6) | 4.59 | -0.17 (3.5) | 5.06 | 0.30 (6.3) | 8.43 | 3.67 (771) |
| 2.44 ^{c)} | 2.10 | -0.34 (13.9) | 3.61 | 1.17 (47.9) | 3.16 | -0.72 (29.5) | 6.52 | 4.08 (167.2) |
| 0.1 mg/ml 3-NT content [wt.%) in the MNT mixture | | | | | | | | |
| Calculated amount | Based on calibration using the IS method | | | | Based on the percentage MNT areas | | | |
| | GC/FID | Error ^{d)} (BW) ^{e)} | GC/MS | Error ^{d)} (BW) ^{e)} | GC/FID | Error ^{d)} (BW) ^{e)} | GC/MS | Error ^{d)} (BW) ^{e)} |
| 4.76 ^{a)} | — ^{f)} | — | 5.50 | 0.74 (5.0) | — | — | 4.58 | -0.18 (3.7) |
| 0.95 ^{b)} | — | — | 0.88 | -0.08 (8.4) | — | — | 1.81 | 0.86 (90.5) |
| 0.49 ^{c)} | — | — | 0.64 | 0.15 (30.6) | — | — | 1.38 | 0.89 (181.6) |

Notes:

^{a)} 2-NT and 4-NT at 1 mg/ml; ^{b)} 2-NT and 4-NT at 5 mg/ml; ^{c)} 2-NT and 4-NT at 10 mg/ml; ^{d)} absolute difference between the determined and calculated value. ^{e)} BW is a relative error expressed as a percentage, also referred to as the percentage error, ^{f)} at 0.1 mg/ml 3-NT, no visible chromatographic peak was observed using the GC/FID method

For samples containing 2-NT and 4-NT at 5 and 10 mg/ml and 3-NT at 0.1 mg/ml, only the GC/MS method was used. For GC/FID, no distinguishable chromatographic peaks were identified at 0.1 mg/ml and the method has not been used in this part of the study. For the GC/MS method, 3-NT content at 0.1 mg/ml was determined with the required accuracy at the lowest 2-NT and 4-NT concentration (1 mg/ml), the relative error being below 5.0%. This applies both to the calibration curve method and the percentage area method.

4. Summary

- ◆ Calibration curves using the IS (PNA) were used in the quantitative determination of MNTs using the GC/FID and GC/MS methods. For the GC/FID method, a calibration curve for the MNT concentration range between 0.5 and 10 mg/ml was determined using the linear regression method. For the GC/MS method, within the concentration range between 0.1 and 10 mg/ml, the calibration points could not be fitted using the linear regression method, particularly at higher MNT concentrations. The data were analysed by fitting a curve using non-linear regression – at least a quartic polynomial. This behaviour of the MS detector has been discussed in literature. To simplify further quantitative determinations, data for the GC/MS within the concentration range between 0.1 and 10 mg/ml were fitted using the linear regression method and three calibration lines, i.e. for 0.1-1.5 mg/ml, 1.5-4.0 mg/ml, and 4.0-10 mg/ml.
- ◆ Using regression parameters (slopes of calibration curves, residual standard deviations and standard deviations of the absolute term), limits of detection (LOD) and quantification (LOQ) of both methods were determined. The LOD and LOQ values, allowing for measurement uncertainties, were identical for both chromatographic methods.

- ◆ The study showed that small amounts of 3-NT can be determined in the presence of a significant excess of other MNTs; 10- to 100-fold excesses were used in the study. For example, it was shown that for 0.5 mg/ml 3-NT, its content can be determined against a 2- to 5-fold excess of 2-NT and 4-NT, both using the calibration curves and based on IS normalisation. For 0.1 mg/ml 3-NT, its content can be determined with high accuracy using the GC/MS method against a 10-fold excess of 2-NT and 4-NT only. The problems related to the quantitative determination of MNTs which may occur during analysis of the products of the first stage of toluene nitration, are due to the fact that the 3-NT content is determined in the lower range of the calibration curves and the 2-NT and 4-NT content – in the upper range of the calibration curves. Within those quantitative determination ranges, the measurement uncertainties may be high, and combining the results may generate significant errors.

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