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# Direct quantification of PAHs and nitro-PAHs in atmospheric PM by thermal desorption gas chromatography with electron ionization mass spectroscopic detection

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## **Abstract**

In this work, we developed and optimized a method for the analysis of PAHs and nitro-PAHs in atmospheric particulate matter (PM) samples by using thermal desorption gas chromatography coupled with electron ionization single quadrupole mass spectrometry (TD-GC-(EI)-MS). The method uses thermal desorption from a PM on a filter sample as means of sample introduction to a column and obviates the need for complex extraction procedures, which are time-consuming and require environmentally unfriendly solvents. Moreover, the possibility of systematic errors is minimized and a significantly smaller amount of sample is required compared to traditional techniques requiring pre-extraction step (approx. 10-times). Thirteen PAHs and three nitro-PAHs were used during method development. Although Tenax cartridges are typically used to capture volatile pollutants from the air, we found that glass-wool liner is the most suitable trap for the examined analytes after desorption from a quartz filter. Among the various instrumental parameters which were tested and optimized, TD desorption flow and hold time, and temperature of the cooled injection system (CIS) proved to be most critical. We also found out that the matrix effect is especially pronounced in the case of high PM loadings, which should be kept in mind when planning the analysis. After the optimization, standard reference materials (ERM-CZ100 and NIST 1648a) were used for partial method validation and finally, real PM<sub>10</sub> and PM<sub>2.5</sub> samples from two Slovenian cities were successfully analyzed.

**Key words:** nitrated polycyclic aromatic hydrocarbons, particulate matter, TD-GC-MS, air pollution monitoring, green analytical method

## 1. [Introduction](#)

Polycyclic aromatic hydrocarbons (PAHs) are common and predominant primary atmospheric pollutants whose increased concentration (indoor and outdoor) affects air quality and our health [1]. Usually, airborne PAHs are formed and directly emitted during the incomplete combustion of fossil fuels and biomass [2,3]. Due to their relatively long atmospheric lifetime (hence long-range transport) and high photochemical reactivity with atmospheric oxidants, primary PAHs often transform into even more toxic secondary organic pollutants, such as nitrated PAHs (nitro-PAHs) [4–6]. PAHs and nitro-PAHs can be detected in the gaseous phase and particulate matter (PM) [7–9]. Those found in PM typically have four or more fused benzenoid rings and are semi-volatile [10]. PAH concentrations are regulated in PM<sub>10</sub> [11], although most primary and secondary PAHs are found in smaller PM below 2.5 μm [12,13].

Chromatographic techniques, such as gas and liquid chromatography (GC/LC), are usually employed when resolving the composition of complex environmental samples. Air quality management has already introduced a standard gas chromatography-mass spectroscopy (GC-MS) method for determining total PAHs in ambient PM<sub>10</sub> collected on a filter (SIST EN 15549 and SIST ISO 12884). Yet, a standard method for nitro-PAHs does not exist. The sample preparation step almost always starts with extraction, which is laborious, requires toxic solvents (harmful to the environment and human health [14]), and can quickly induce errors [15]. Besides, a large amount of PM is required for the analysis due to sample dilution. Some effort has already been made to improve or avoid the lengthy extraction process and improve the sensitivity of PAH determination in ambient PM and other environmental samples [16–19].

A greener and simplified option is to use thermal desorption (TD) prior to the GC-MS analysis. The TD is an extraction technique based on precise sample heating to the temperature at which target analytes are desorbed from a sample matrix. Desorbed analytes are first collected on a cooled trap and later quickly desorbed and transported to the column with a carrier gas. Although the desorption parameters have been optimized for parent PAHs several times, various critical steps have been identified by different groups [20–25], which calls for special attention to the instrument usage and method validation. Moreover, only a few attempts exist in the literature to analyze nitro-PAHs by thermal desorption gas chromatography with mass spectroscopic detection (TD-GC-MS) [23,26]. They either use chemical ionization GC-MS or two-dimensional GC and MS/MS detection, which are not common instrumentation for air quality laboratories.

This work focuses on the optimization and validation of a simple TD-GC-MS method with an electron ionization (EI) single quadrupole detector for the direct analysis of nitro-PAHs and their analogous

non-nitrated PAHs in ambient PM samples collected on quartz fiber filters. We examined a vast instrument parameter space, including different columns, trap liners, flow rates, and temperatures for the best analyte separation, optimal sensitivity, and repeatability. The developed method was partially validated by two standard reference materials (SRM) and compared to the existing method (SIST EN 15549 and SIST ISO 12884) for determining total PAHs in ambient PM based on extraction and by using liquid injection GC-MS. Nine real PM<sub>10</sub> samples from Nova Gorica, Slovenia, obtained from the Slovenian Environment Agency (ARSO) were re-analyzed with the newly developed method. The new method was also used to analyze our PM<sub>2.5</sub> samples collected in the city of Ljubljana, Slovenia, in winter and spring 2021.

## 2. [Materials and Methods](#)

### 2.1. Chemicals

A US Environmental Protection Agency (EPA) 525 PAH Mix B (Sigma-Aldrich Chemie GmbH) containing acenaphthylene (Acy), anthracene (Ant), benz[a]anthracene (BaA), benzo[b]fluoranthene (Bbf), benzo[k]fluoranthene (Bkf), benzo[ghi]perylene (Bgp), benzo[a]pyrene (Bap), chrysene (Cry), dibenz[a,h]anthracene (DbA), fluorene (Flu), indeno[1,2,3-cd]pyrene (Ind), phenanthrene (Phe), pyrene (Pyr) at 500 µg mL<sup>-1</sup> of each component in acetone was used as a multi-reference standard for PAH compounds (PAH mix).

BCR<sup>®</sup> certified standard materials: 9-nitroanthracene (9nA), 6-nitrochrysene (6nC) and 1-nitropyrene (1nP) were used for the preparation of stock solutions of nitro-PAHs which were of similar concentrations to the PAH mix. Each purchased solid standard was dissolved in acetone (GC-MS grade, Supelco) to obtain 500 µg mL<sup>-1</sup> and stored in a freezer at -20 °C before use.

Physico-chemical properties of the analytes important for the TD-GC-MS method optimization are gathered in Table 1. Benzo(a)pyrene-d<sub>12</sub> (Sigma-Aldrich Chemie GmbH) was further used as an internal standard (IS) to follow the stability of GC-MS.

Two standard reference materials (SRM): Environmental Resources Management (ERM<sup>®</sup>) - CZ100; Fine dust (PM<sub>10</sub>-like) (from now on ERM) and National Institute of Standards and Technology (NIST) 1648a; Urban Particulate Matter (from now on NIST) were used for partial method validation.

Table 1 Physico-chemical properties, selected ions for MS detection and retention times of 13 PAHs and 3 nitro-PAHs along with the obtained limits of detection (LOD), limits of quantification (LOQ) and relative standard deviation (RSD) of repetitive measurements by the developed TD-GC-MS method.

|                        | Target compound      | Short name                      | Mol. formula                                    | M.W.  | b.p., °C | Target ion, m/z | Qual. ion, m/z | SIM group* | RT, min | LOD, ng | LOQ, ng | RSD, % | NIST 1648a | ERM-CZ100 |
|------------------------|----------------------|---------------------------------|---|-------|----------|-----------------|----------------|------------|---------|---------|---------|--------|------------|-----------|
| PAHs                   | Acenaphthylene       | Ace                             | C <sub>12</sub> H <sub>8</sub>                  | 152.2 | 265      | 152             | /              | 1          | 10.6    | 0.053   | 0.18    | 14     |            |           |
|                        | Fluorene             | Flu                             | C <sub>13</sub> H <sub>10</sub>                 | 166.2 | 295      | 166             | 165            |            | 11.5    | 0.021   | 0.069   | 23     |            |           |
|                        | Phenanthrene         | Phe                             | C <sub>14</sub> H <sub>10</sub>                 | 178.2 | 340      | 178             | /              | 2          | 12.7    | 0.040   | 0.13    | 9.3    | ✓          | ●         |
|                        | Anthracene           | Ant                             | C <sub>14</sub> H <sub>10</sub>                 | 178.2 | 340      | 178             | /              |            | 12.8    | 0.042   | 0.14    | 27     |            | ●         |
|                        | Pyrene               | Pyr                             | C <sub>16</sub> H <sub>10</sub>                 | 202.3 | 404      | 202             | 101            | 3          | 14.8    | 0.011   | 0.033   | 3.5    | ✓          | ●         |
|                        | Benzo(a)anthracene   | Cry                             | C <sub>18</sub> H <sub>12</sub>                 | 228.3 | 448      | 228             | 114            | 4          | 16.7    | 0.006   | 0.019   | 8.4    | ✓          | ✓         |
|                        | Chrysene             | BaA                             | C <sub>18</sub> H <sub>12</sub>                 | 228.3 | 437      | 228             | 114            |            | 16.7    | 0.015   | 0.049   | 7.4    | ✓          | ●         |
|                        | Benzo(b)fluoranthene | BbF                             | C <sub>20</sub> H <sub>12</sub>                 | 252.3 | 481      | 252             | 126            | 5          | 18.3    | 0.007   | 0.023   | 15     |            | ✓         |
|                        | Benzo(k)fluoranthene | BkF                             | C <sub>20</sub> H <sub>12</sub>                 | 252.3 | 481      | 252             | 126            |            | 18.3    | 0.008   | 0.026   | 14     | ✓          | ✓         |
|                        | Benzo(a)pyrene       | BaP                             | C <sub>20</sub> H <sub>12</sub>                 | 252.3 | 495      | 252             | 126            |            | 18.7    | 0.019   | 0.063   | 16     | ✓          | ✓         |
| Indeno(1,2,3-cd)pyrene | Ind                  | C <sub>22</sub> H <sub>12</sub> | 276.3   | 536   | 276      | 138             | 6              | 20.1       | 0.049   | 0.16    | 23      | ✓      | ✓          |           |
| Dibenz(a,h)anthracene  | DbA                  | C <sub>22</sub> H <sub>14</sub> | 278.4   | 524   | 278      | 139             |                | 20.2       | 0.064   | 0.21    | 22      |        | ✓          |           |
| Benzo(g,h,i)perylene   | Bgp                  | C <sub>22</sub> H <sub>12</sub> | 276.3   | 550   | 276      | 138             |                | 20.5       | 0.059   | 0.20    | 25      | ✓      | ●          |           |
| nitro-PAHs             | 9-nitroanthracene    | 9nA                             | C <sub>14</sub> H <sub>9</sub> NO <sub>2</sub>  | 223.2 | 275      | 223             | 193            | 7          | 14.9    | 0.009   | 0.030   | 6.5    | ✓          |           |
|                        | 1-nitropyrene        | 1nP                             | C <sub>16</sub> H <sub>9</sub> NO <sub>2</sub>  | 247.3 | 390      | 217             | 189            | 8          | 17.5    | 0.064   | 0.21    | 23     | ✓          |           |
|                        | 6-nitrochrysene      | 6nC                             | C <sub>18</sub> H <sub>11</sub> NO <sub>2</sub> | 273.3 | 505      | 243             | 273            | 9          | 18.9    | 0.20    | 0.65    | 20     |            |           |

\*Groups of ions measured simultaneously in particular time frames: dwell times corresponding to each m/z are gathered in Table S1.

## 2.2. TD-GC-MS

The method optimization and analyses were performed by a GC (Agilent Technologies: 7890B GC System) coupled to a single quadrupole MS (Agilent Technologies: 5977B MSD) with EI, which is equipped with a TD unit (Gerstel, TD3.5+) and a cooled injection system (CIS) (Gerstel, CIS4) as means of a sample introduction system. Two Agilent J&W columns were tested as a stationary phase for the separation of selected PAHs: a non-polar HP-5ms column ((5%-phenyl)-methylpolysiloxane, 30 m x 0.25 mm x 0.25  $\mu$ m) and a mid-polar DB-EUPAH column (diphenyl-/dimethylpolysiloxane (50%/50%) modified with an aromatic selector, 30 m x 0.25 mm x 0.25  $\mu$ m), the latter being specially designed on demand of the European Environmental Agency for the separation of EU regulated PAHs. The mobile phase – a carrier gas was helium (Messer Group) with purity greater than 99.9999 %.

For the method optimization, one-eighth portions (1/8) of a quartz fiber filter (Pall, 47 mm diameter) were spiked with 10  $\mu$ L of a standard mix solution containing PAHs and nitro-PAHs (hereafter standard filters). Every standard filter was left for approximately 2 min to dry at ambient conditions and then set in a TD glass tube (Desorption tubes for GESTEL – TD3.5+).

During the analysis, analytes are first desorbed from a filter sample in a TD glass tube and travel with a carrier gas to the CIS unit where they get trapped due to the low temperature maintained. Three different CIS liners were tested in this study: baffled (activated), and Tenax and a glass wool (both deactivated) liners (all GERSTEL CIS4/TDU/TD3.5+). Deactivated liners were tested at their maximum temperature of 275 °C, while the baffled liner was tested at the same maximum temperature as of the TD (320 °C). The second, more rapid desorption is performed from a CIS liner, from where the desorbed analytes are flushed directly to the GC column.

In the present study, different instrumental parameters such as gas flow rates, temperatures, and transfer times were optimized for both systems, TD and CIS, which is schematically represented in Fig. 1. Temperature ramps were fixed at 60 °C min<sup>-1</sup> for TD and 720 °C min<sup>-1</sup> for CIS. The CIS trap was set at the lowest temperature possible (5 °C). The system allows for different injection modes at both desorption steps; splitless or split mode can be applied at TD or CIS. Since our aim was to detect trace analyte concentrations, splitless and low-split configurations were tested: splitless and split 1-4 options on CIS only were compared.

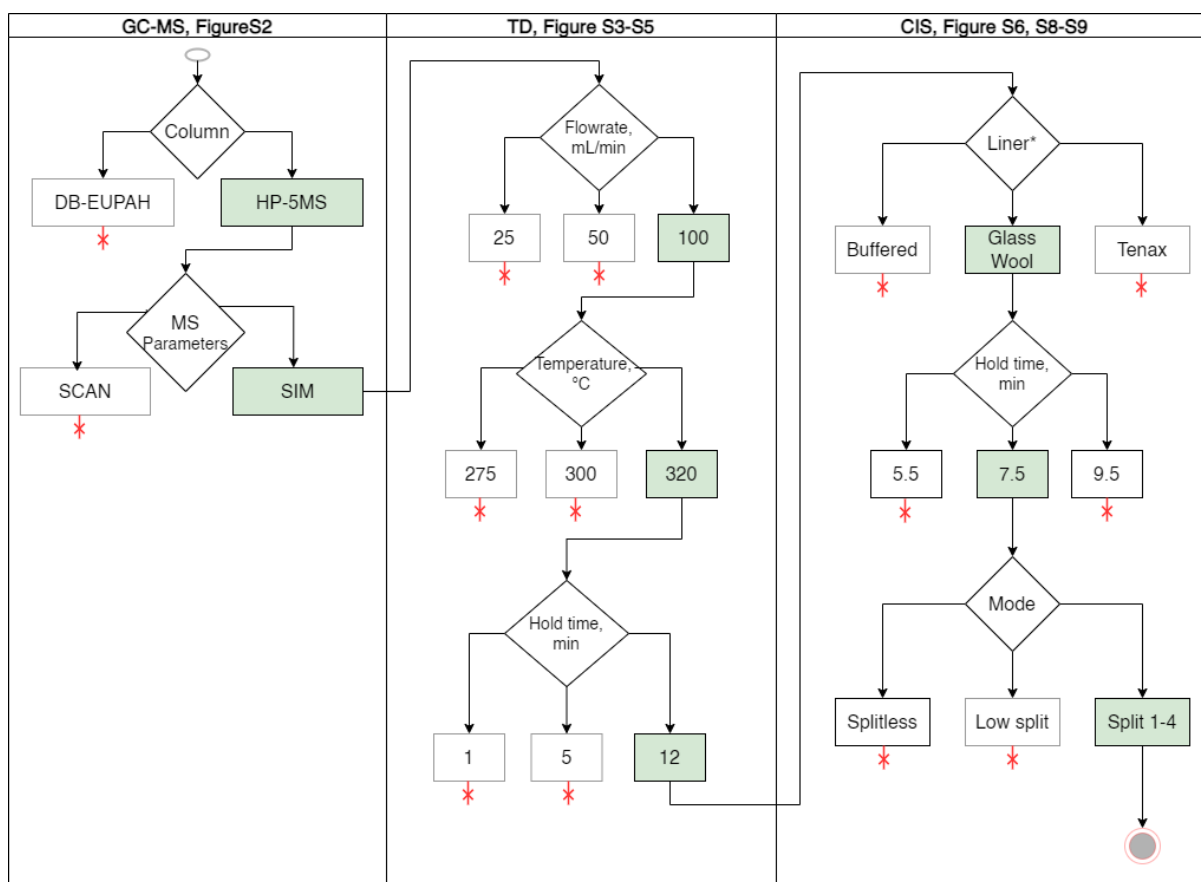


Figure 1 Workflow diagram for the optimization of TD-GC-MS method: GC-MS parameters were optimized first with a liquid standard solution (left panel), followed by TD and CIS parameters optimization (middle and right panel, respectively). Trap temperature was always held at 5 °C due to system limitations.

The chromatographic conditions from the existing Agilent application note were used [27] and slightly adapted to our operating conditions. The oven temperature program started at 55 °C, where it was initially held for 7 min, followed by a temperature increase to 170 °C at 25 °C min<sup>-1</sup> and further to 325 °C at 15 °C min<sup>-1</sup>. The final temperature of 325 °C was held for 3 min before the oven started cooling down.

Selected ion monitoring (SIM) mode was used to detect and quantify ultra-trace nitro-PAHs in real PM samples. Peak identification and target ion selection were made based on a scan chromatogram of a standard mix and integrated library search (2017 NIST MS Library). To achieve the best sensitivity, selectivity, and assure accuracy and repeatability of the method, two fragment ions were chosen for every compound of interest (the most abundant and another one for identification). The run time was split into nine groups, described in Table 1.



### 2.3. Statistical analysis and validation

Calibration curves were constructed in the range of 10–5000 pg filter<sup>-1</sup> of each compound, spanning over the expected analyte concentration in atmospheric PM samples. Every standard filter was measured two times and in random order. No peak corresponding to the target analytes was detected in blank filters. Therefore, the limit of detection (LOD) and the limit of quantification (LOQ) were calculated from the standard deviation (SD) of ten repetitions of the lowest concentration standard filter, with  $LOD = 3.28 \times SD$  (95 % confidence) and  $LOQ = 10 \times SD$  [28].

Linearity was tested by comparing variances of low (0.1 ng) and high (5 ng) concentration standard filters with use of a statistical F-test (equation 1), i.e. to find out whether the calibration curve is homoscedastic or not.

$$F = \frac{SD_{max}^2}{SD_{min}^2} \quad 1$$

$SD_{max}^2$  is the square of SD of the high concentration sample, while  $SD_{min}^2$  is the square of SD of the low concentration sample [28]. Every analyte concentration was measured five times.

The method was further validated using two SRMs for ambient PM. Based on the expected and obtained values, method's accuracy and repeatability (3 repetitions) were assessed.

Since matrix may induce signal suppression or enhancement, the impact of the matrix effect was also investigated. For this purpose, a real atmospheric PM sample was spiked with a standard solution corresponding to 5 ng loading per analyte and measured three times with and without spiking.

### 2.4. Sample collection

PM<sub>10</sub> samples were collected by ARSO on quartz fiber filters (Pall, 150 mm diameter) in Nova Gorica, Slovenia, in 2021 (2.-5. March and 22.-26. April). Samples were collected for 24 h using a high volume sampler (Digital DHA-80 Aerosol Sampler, Switzerland), with a flow rate of 500 L min<sup>-1</sup>. PM<sub>2.5</sub> samples were collected on quartz fiber filters (Pall, 47 mm diameter) at the National Institute of Chemistry in Ljubljana, Slovenia, in winter 2021 (24.-28. February) and spring 2021 (24.-28. May). Ambient air was drawn through every filter for 24 h with a constant flow of 2.3 m<sup>3</sup> h<sup>-1</sup> using a low-volume PM sampler (Giano, Dado lab). Both sampling sites are shown in Fig. S1.

Before and after sampling, PM<sub>2.5</sub> filters were conditioned for at least 24 h at constant temperature (22 ± 1 °C) and humidity (50 ± 5 %) to allow for the determination of exact PM masses. PM loadings of these samples are shown in Table S4. After weighing, the PM<sub>2.5</sub> filters were packed air-tight and stored

in a freezer at -20 °C until analysis, while PM<sub>10</sub> were kept at room conditions. The same amount of a sample, i.e., 1/8 filter, was taken for analysis every time.

### 3. [Results and Discussion](#)

For the purpose of method optimization, the performance of two different Agilent columns was first compared using a standard liquid injection mode. From the chromatogram depicted in Fig. S2, the DB-EUPAH column assures better separation of critical PAH isomers, i.e., BbF, BjF and BkF, which is in line with its specifications [29]. However, the HP-5MS column allows a shorter time for the satisfactory separation of our 16 target analytes (Fig. S2) and was chosen for further optimization.

#### 3.1. [TD parameters optimization](#)

The literature on TD-GC-MS analysis of compounds with similar chemical properties was reviewed to find an optimal set of instrumental parameters for accurate quantification of the target analytes in complex environmental samples. Although there have been a few attempts of semi-volatile PM components analysis by TD-GC-MS, the literature contrasts with different conclusions regarding the critical steps that must be carefully considered. While some authors underline the importance of the desorption temperature [24], others pointed out that high sample loading can compromise accurate analyte determination [22].

Standard filters with 2 ng of each analyte were used for instrumental parameters optimization. Comparative diagrams of method performance at different optimization steps are shown in SI (Fig. S3-S6). Independently of the examined parameters, signal responses of the first two peaks (*Ace and Flu*) were always lower compared to the signals of the other compounds. However, in the case of liquid injection, the signal intensities of *Ace* and *Flu* were comparable for all analytes. The obtained low signals for *Ace* and *Flu* in the case of TD analysis can be attributed to the loss due to the combination of high TD desorption flow and relatively high trap temperature (5 °C).

On the other hand, the analytes with high boiling points (lower volatility) required maximum desorption temperature and time, and high gas flow rates for sufficient desorption. They also seem to be efficiently trapped on a cooled CIS liner. We finally found out that despite the lower maximal desorption temperature (i.e. 275 °C), deactivated glass wool liner exhibited the best performance, probably due to its large surface area, which allows the analytes to adsorb more efficiently.

Hence, the optimal thermal desorption at TD was set to 17 min - with a heating rate of 60 °C min<sup>-1</sup> (from 30 °C to 320 °C) and additional hold time of 12 min. As already mentioned, the maximum temperature at CIS was constrained with the glass wool liner at 275 °C, which was compensated with a longer desorption time, i.e., 7.5 min, the heating rate was 12 °C s<sup>-1</sup>. Although one could expect this

would cause substantial peak broadening, this was not the case due to the applied delay in the column heating program. A time diagram of optimal temperatures and flow rates during the analysis is shown in Fig. 2 and the chromatogram obtained with the optimized TD conditions is shown in Fig. S7.

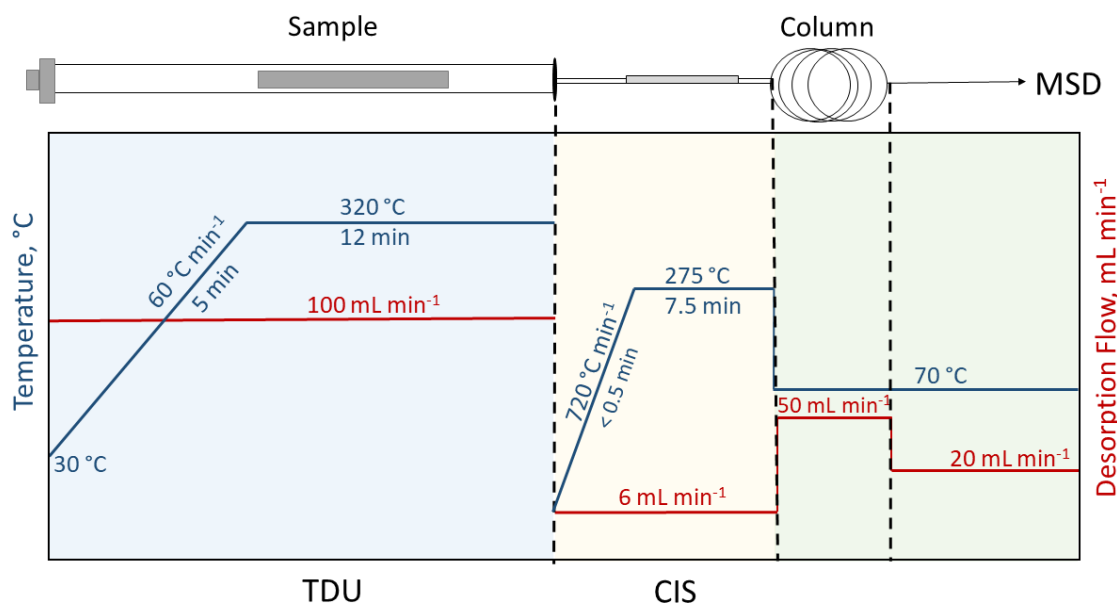


Figure 2 Optimized instrumental parameters of the thermal desorption unit: temperature and carrier gas flow time diagram for TD and CIS desorption. The blue square presents TD desorption, while yellow presents CIS desorption and initial time to the GC column at the same time. The sample was set in a liner depicted in grey at the top of the graphic. The purge of CIS during chromatographic separation is shown in the green square.

We further compare different injection modes in Fig. S8. Although split 1-4 resulted in roughly half-lower sensitivity than the splitless mode, the split mode was chosen to prevent the column from too large amounts of impurities that would be loaded in the case of real PM samples. Moreover, the split mode facilitates the desorption from the CIS by the increased carrier gas flow rate, which allows for shorter desorption (and analysis) times and prevents from too long retention of sample components at the inlet of the column.

### 3.2. Measuring range, linearity, LOD and LOQ

Visually, linear response was assessed in the observed concentration range for all target analytes (Pearson regression coefficients ( $R^2$ ) were in the range of 0.9668-0.9999). Exemplary calibration curves for 1nP and BaP are shown in Fig. S8. The results pertaining to the homoscedasticity testing are shown in Table S2. The calculated  $F_{cal}$  value ( $p=0.05$ ; equation 1) is greater than the theoretical  $F_{teor}$  value, which indicates heteroscedasticity for all investigated compounds in the

measured mass range. Therefore, weighted linear regression ( $1/x$ ) was applied for quantification purposes.

LOD and LOQ as determined for each analyte are summarized in Table 1. According to the obtained results, the LODs for PAHs were in the range of 6–64  $\text{pg filter}^{-1}$ , comparable to or lower than in the reviewed literature where TD-GC-MS with EI ionization was used [20,22,24]. The determined LODs for nitro-PAHs are somewhat higher, i.e., in the range of 9–264  $\text{pg filter}^{-1}$ , also compared with other literature where chemical ionization MS was applied [26]. To our knowledge, nitro-PAHs analysis by EI-MS has never been successfully performed so far. Up until now, negative chemical ionization has been exclusively used for the ionization of nitro-PAHs [26,30].

### 3.3. Accuracy testing using standard reference materials and real $\text{PM}_{10}$ samples

Two SRMs for ambient PM (ERM and NIST) were used for the accuracy assessment of the developed TD-GC-MS method. Note that only NIST specifies secondary nitro-PAHs, which are in the focus of this study. Each SRM was measured three times using less than 0.5 mg material in every repetition. The aim was to keep the analyzed particulate mass (i.e., the mass of the standard) within the range of PM masses deposited on filters in typical ambient measurements. However, the standards used do not guarantee homogeneity at this level, which must be taken into account when interpreting the results. Inaccuracy of weighing, which is estimated at a maximum of 10 %, could also affect the analysis and result in larger deviations. Average, minimum, and maximum measured analyte concentrations in each standard are shown and compared with the specified values in Fig. 3.

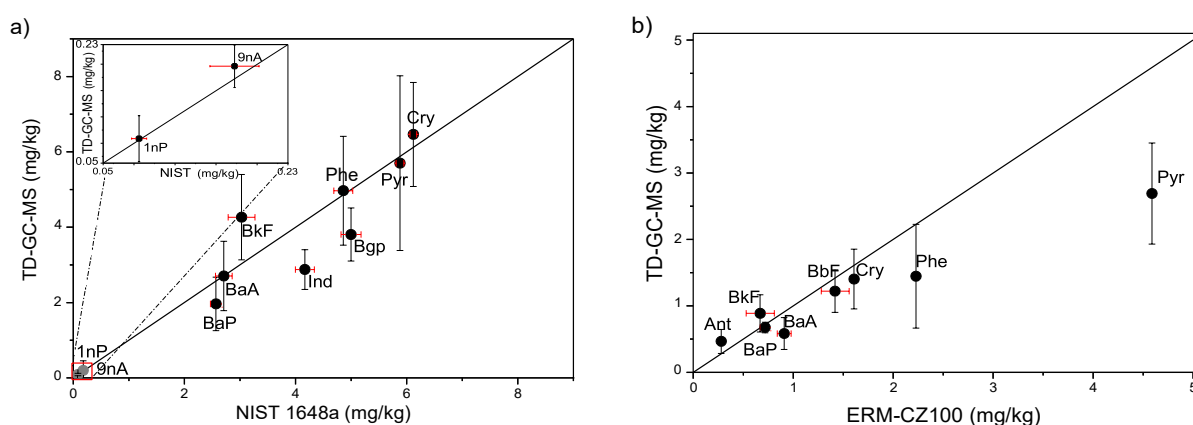


Figure 3 A comparison of the new TD-GC-MS method with certified values of reference materials: a) NIST, b) ERM. Every data point represents an average value of three repetitions. Uncertainty is shown with red (SRM) and black (this study) error bars.

In the case of NIST (Fig. 3a), good agreement was achieved for most analytes (including nitro-PAHs), except for BkF, Ind and Bgp. BkF is the only overestimated compound, which could be due to Bjf interference as the two analytes cannot be separated on the HP-5MS column. Notwithstanding, in the case of ERM (Fig. 3b), BkF agrees well with the specified value. On the other hand, Ind and Bgp were strongly underestimated in NIST, whereas we could not detect them in ERM at all. This could be due to their extremely high boiling points, which makes them elute at the end of the chromatogram, resulting in broader peaks than of the other analytes and thus poorer sensitivity and measurement precision. While the measured concentrations of Phe and Pyr are in agreement with the certified values in NIST, their concentrations in ERM were low, which was evident in multiple analyses (e.g. see Fig. S9). Especially for Pyr, a very large spread of data was obtained (refer here also to RSD in Table 1). Although confidence is typically reported together with certified values, it is not true for these two analytes from the additional material information, which could also be a potential source of error.

Nine ambient PM<sub>10</sub> samples, which had already been analyzed for the content of PAHs by a liquid extraction method using a solvent mixture of hexane and acetone (1:1), were additionally measured. For the conventional method with liquid extraction, 2215 mm<sup>2</sup> filter area was used, whereas a ten times smaller amount of filter (217 mm<sup>2</sup>) was sufficient for our analysis (and could be even reduced). In Table 2 and Table S3 the results of both analyses are compared. Note that concentrations in ng m<sup>-3</sup> are given, which are typically used in air quality control.

Table 2 Quantification of PAHs in PM<sub>10</sub> samples collected in Nova Gorica in March and April 2021. Five samples from each campaign were analyzed and monthly average values as determined by liquid extraction (ARSO) and our method (TD-GC-MS) are compared.

| PAH         | March                           |                             |                  | April                           |                             |                  |
|-------------|---------------------------------|-----------------------------|------------------|---------------------------------|-----------------------------|------------------|
|             | TD-GC-MS,<br>ng m <sup>-3</sup> | ARSO,<br>ng m <sup>-3</sup> | Difference,<br>% | TD-GC-MS,<br>ng m <sup>-3</sup> | ARSO,<br>ng m <sup>-3</sup> | Difference,<br>% |
| BaA         | 0.72±0.06                       | 0.992                       | -27.4            | 0.098±0.007                     | 0.090                       | 8.9              |
| BbF and BkF | 2.1±0.3                         | 3.415                       | -38.5            | 0.46±0.07                       | 0.541                       | -14.9            |
| BaP         | 0.58±0.09                       | 1.285                       | -54.9            | 0.14±0.03                       | 0.188                       | -25.5            |
| Ind         | 0.12±0.01                       | 0.208                       | -42.3            | <LOD                            | <LOD                        | n.a              |
| DbA         | 0.42±0.1                        | 1.330                       | -68.4            | 0.29±0.06                       | 0.238                       | 21.8             |

By examining the obtained data, one could conclude that the agreement between our TD-GC-MS and ARSO analyses is somewhat poor. However, 20 % confidence obtained for less polluted samples is within the acceptable range for PM filters due to their heterogeneity, which is supported by the determined repeatability reported in Table 1. A similar conclusion was also made in another study

where a similar method was used to analyze PAHs in PM [22]. Moreover, a few other facts could also influence the obtained results; (i) the filters were not analyzed immediately after their collection by TD-GC-MS; meanwhile being stored at room temperature, which could have resulted in a loss of relatively volatile analytes, (ii) the extraction method does not report measurement uncertainty to be considered in data evaluation. Furthermore, in the literature review, some authors suggest that suppression of the peak signal (up to approximately 20 %) is possible due to the matrix effect if individual internal standards are not used for each analyte specifically [31]. Note that ARSO indeed performed their analyses with appropriate internal standards, while we did not have them.

### 3.4. Matrix effect

In the next step, we tested the matrix effect with liquid standard addition to the matrix, i.e. ambient PM<sub>2.5</sub> sample. The matrix can influence analyte desorption from a filter due to analyte interaction with the remaining PM, CIS liner performance, where more volatile components from PM occupy active sites of the liner and the target compounds might get lost. The matrix can also affect separation characteristics of the column (poorer separation and delayed retention with peak broadening), and ionization efficiency at the detector.

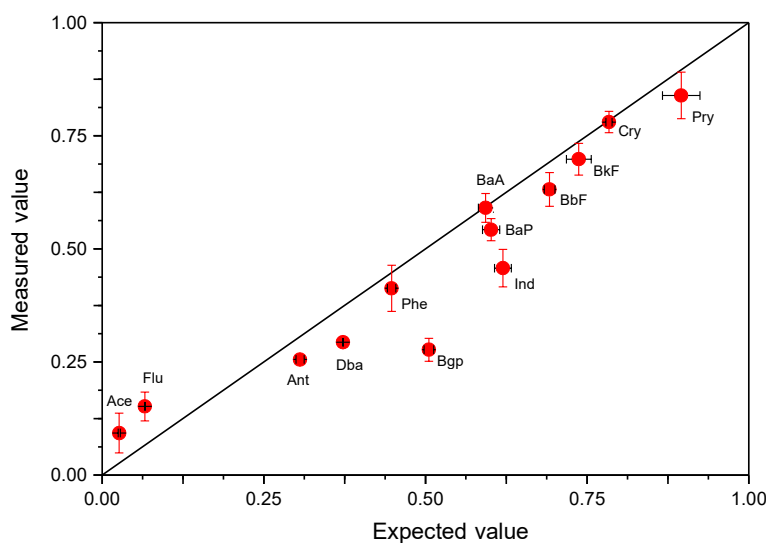


Figure 4 Matrix effect for real PM<sub>2.5</sub> samples spiked with 5 ng/analyte standard PAH Mix. Relative average signal intensity of three repetitions and SD are shown.

Fig. 4 shows a comparison between the expected and measured values for thirteen PAHs. In general, matrix effect was not confirmed by the performed t-test, which resulted in lower t-value (0.482) compared to the critical value at 95 % confidence (1.711). Positive deviations were obtained only for the most volatile two compounds with three benzene rings (Ace and Flu). On the other hand, the

major deviation was again observed for Ind and Bgp. These two compounds were also critical during accuracy testing, and the matrix effect can explain the obtained results.

### 3.5. Measurement of real samples

Ten PM<sub>2.5</sub> filter samples (5+5) were collected in February and May 2021 in Ljubljana, Slovenia, and successfully analyzed for PAHs (13) and nitro-PAHs (3) by the developed method. In winter, the average PM<sub>2.5</sub> mass concentration was 27 µg m<sup>-3</sup>, while for the spring period, it was considerably lower (7 µg m<sup>-3</sup>). A similar trend was also observed for the total mass concentration of target analytes (11.2 ng m<sup>-3</sup> and 0.86 ng m<sup>-3</sup> in winter and spring, Table S4), consistent with other investigations in several central European cities [9,32].

Fig. 5 shows seasonal variation of PAHs and nitro-PAHs in PM<sub>2.5</sub>. For all samples, PAHs with three benzene rings (Ace, Flu, Phe, Ant) made up less than 5 % of the total PAHs and nitro-PAHs in PM<sub>2.5</sub>. These compounds are more volatile than the others and are mostly distributed in the gas phase [33]. Moreover, it is also easier to lose these compounds during sample storage. It was further noticed that BaA, Cyr and BaP provided a larger contribution (%) to the fraction of PAHs and nitro-PAHs in PM<sub>2.5</sub> during the winter, which indicates that coal combustion is a possible source of these pollutants [34]. On the other hand, Fluo, Phe, Ant, BbF, and Ind were more dominant during the spring period, which may be connected with biomass burning during agricultural activities.

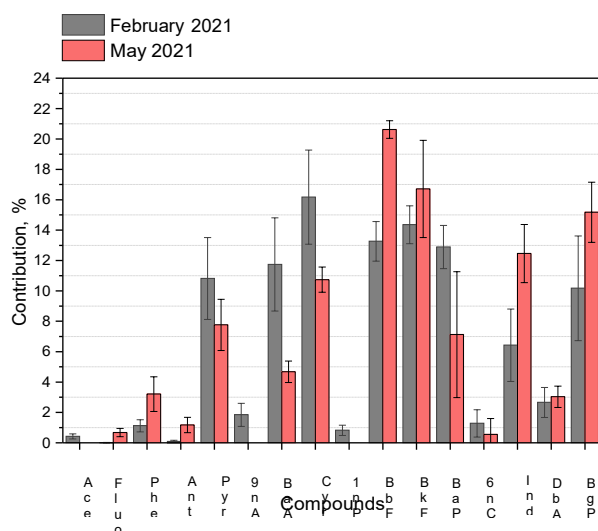


Figure 5 Average composition profile of PAHs and nitro-PAHs collected in PM<sub>2.5</sub> in winter – February 2021 (grey columns) and spring – May 2021 (red columns); % of a sum of the measured PAHs and nitro-PAHs are shown.

Nitro-PAHs were not detected in spring samples, while the concentration of individual nitro-PAHs in the winter period was less than 0.5 ng m<sup>-3</sup>. The dominant nitro-PAH in winter was 9nA (0.22±0.01 ng m<sup>-3</sup>), which is primarily emitted from diesel engines, coal or biomass burning [35]. It is interesting to

note that in the same period, its non-nitrated analogue (Ant) was mostly not detected in PM<sub>2.5</sub> (it was detected in one single spring sample), suggesting different sources of the two analytes.

Based on the obtained results, the newly developed TD-GC-MS method proves suitable to be successfully applied in source apportionment and other studies that include parent PAHs and their nitrated transformation products.

#### 4. [Conclusion](#)

A direct method using TD-GC-MS was developed and optimized for simultaneous quantification of PAHs and nitro-PAHs in atmospheric PM, without an extraction procedure. The amount of a filter sample required for the analysis was optimized to a minimum – ten times or even smaller filter area is needed than for the conventional method with liquid extraction, which offers the following advantages: i) the rest of the filter can be used for other complementary analyses and ii) shorter sampling times can be applied. Linear response in the range of 10-5000 pg filter<sup>-1</sup> of each analyte was obtained. Due to heteroscedastic characteristics, which were confirmed for all investigated compounds, weighted calibration curves were used for quantification. The LOD for PAHs (6-64 pg filter<sup>-1</sup>) and nitro-PAHs (9-2645 pg filter<sup>-1</sup>) were comparable to or lower than reported in the literature, considering that we used an EI MS detector, which is not commonly used for nitro-PAH determination. Two SRM for ambient PM (NIST and ERM) were used for accuracy assessment and showed good agreement for most analytes, except for compounds with the highest boiling points (Ind and Bgp). For the same two compounds, a significant deviation was found, which is ascribed to the influence of PM matrix. In addition to air quality monitoring, which would need a thorough method validation prior to its wide application, the newly developed TD-GC-MS method can be successfully applied for source apportionment and secondary organic aerosol formation studies, including parent PAHs and their nitrated transformation products, which has rarely been done before.

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## 6. [References:](#)

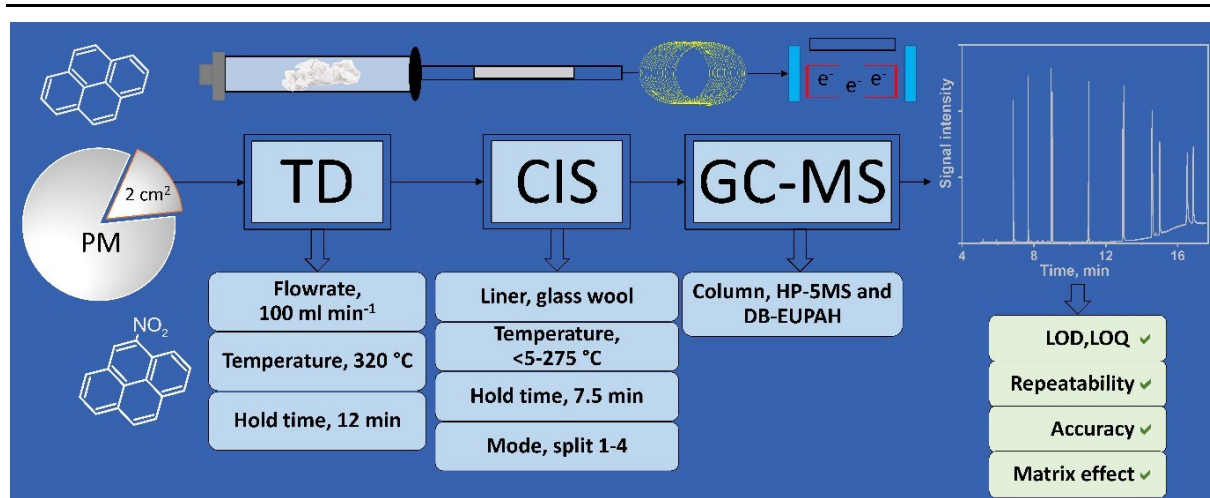
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