

Determination of Nitro-Polycyclic Aromatic Hydrocarbons in Air Particulates Using the Agilent 7000A Triple Quadrupole GC/MS System

Application Note

Environmental

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Abstract

The analysis of nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) in air particulates was performed by capillary GC in combination with the Agilent 7000A Triple Quadrupole GC/MS system (G7010AA) operated in multiple reaction monitoring (MRM) mode. While classical methods for the analysis of nitro-PAHs are based on GC/MS analysis by a single quadrupole in the selected ion monitoring (SIM) mode after labor-intensive sample preparation or on multidimensional GC/MS, direct analysis of the crude air particulate extract could be performed due to the enhanced selectivity of the MS/MS detection mode. Nitro-PAHs could be detected in a real sample at low $\text{pg}/\mu\text{L}$ level, corresponding to pg/m^3 in air samples.



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Introduction

Nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) are among the most toxic, carcinogenic, and mutagenic substances that have been detected in ambient air. Like PAHs, nitro-PAHs are primarily adsorbed on air particulate matter. They can be measured in the particulate fraction sampled at urban locations, typically in the 1 to 100 pg/m³ concentration range. This concentration range is about 100 to 1,000 times lower than for neutral PAHs, such as naphthalene, phenanthrene, pyrene, and benzo(a)pyrene.

The sampling of nitro-PAHs in ambient air is normally done using high-volume samplers, whereby the particulates are trapped on a filter (glass fiber) while the gas phase fraction is sampled on a second filter consisting of polyurethane foam (PUF) or XAD resins downstream of the particulate filter. Next, the filters are liquid extracted (Soxhlet) and the extracts are concentrated. The obtained extracts (typically 1 mL, corresponding to 1,000 m³ air sample) can be analyzed for neutral PAHs, present at µg/mL concentration in the extract. The complexity of the extract and high background from sample matrix, however, do not allow reliable determination of ng/mL concentrations of nitro-PAHs by direct analysis using GC/MS. Therefore labor-intensive sample preparation methods, such as fractionation by normal phase liquid chromatography on an aminopropyl column, or two-dimensional GC using heart-cutting are used.

In this study, the air particulate extract obtained by Soxhlet extraction from a particulate filter was analyzed without additional cleanup using GC/MS/MS on the Agilent 7000 triple quadrupole system, operated in multiple reaction monitoring (MRM) mode.

Experimental

Chemicals and Standards

Pure nitro-PAHs (99 to 97 percent purity) were purchased from Sigma-Aldrich (Bornem, Belgium). Calibration solutions were prepared in toluene. For method setup using Q1-scan mode and for product ion scan, a test solution of 10 ng/µL nitro-PAHs was used.

For calibration in MRM mode, test solutions at 5 to 50 pg/µL were used.

Sampling

Air particulate samples were taken using a high-volume sampler (Anderson Graseby, USA) on glass fiber filters, backed-up with a PUF filter. High-volume sampling is done at 0.9 m³ per minute during 24 hours. These filters were extracted by Soxhlet extraction with dichloromethane and concentrated to 1 mL with solvent exchange to toluene. No additional cleanup was used.

Instrumentation

Analyses were performed on an Agilent 7890A GC system combined with a prototype Agilent 7000A Triple Quadrupole GC/MS system. The GC was equipped with a split/splitless inlet. Separation was performed on a 15 m x 0.25 mm id x 0.25 µm DB-5MSUI column.

Injection (1 µL) was performed in splitless mode at 280 °C. The column was programmed from 70 °C (1 minute) to 310 °C at 20 °C/minute.

The Agilent 7000A QQQ system was equipped with an inert electron impact (EI) source and was operated in MRM mode. Ion source temperature was 300 °C, quadrupole temperatures were 150 °C. The molecular ions were selected as precursor ion and two transitions per target solute were selected. The most important transition was the loss of the nitro-group (M-46). The selected ions are listed in Table 1.

Table 1. Selected Transitions for Analysis

Solute	Precursor ion	Product ions
1-nitro-naphthalene	173	127, 115
9-nitro-anthracene	223	193, 176
3-nitro-fluoranthene	247	201, 217
1-nitro-pyrene	247	201, 217
2-nitro-pyrene	247	201, 217

Results and Discussion

The analysis of a test mixture containing the nitro-PAH test solutes at a 50 pg/µL level is shown in Figure 1. Excellent sensitivity was obtained. The limit of detection for these solutes was around 1 to 5 pg. This value is comparable with data obtained using GC/EI/MS in SIM mode on an Agilent 5975C Series GC/MSD.

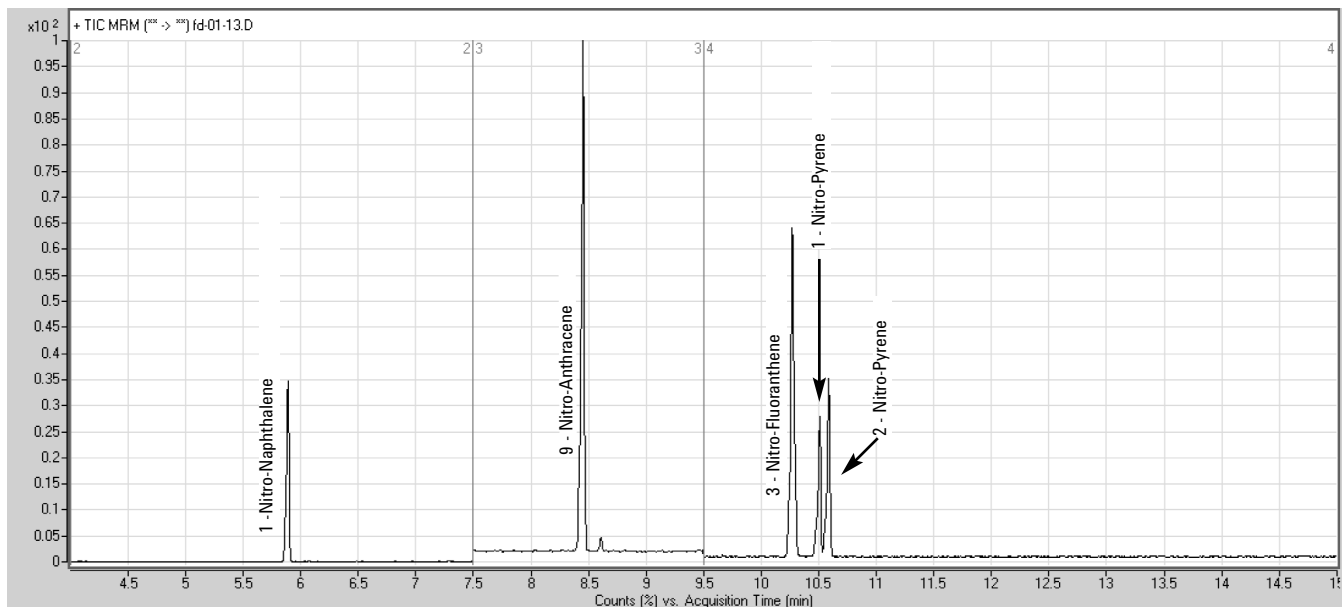


Figure 1. Analysis of nitro-PAH test mixture at 50 pg/μL level using GC/QQQ in MRM mode.

Next, an extract from air particulates collected at an urban location was analyzed. The chromatogram (Figure 2), showing the MRMs for nitro-naphthalene (top), nitro-anthracene (middle), and nitro-fluoranthene, and nitro-pyrene (bottom) clearly show that all test solutes can easily be detected. The concentrations of the nitro-PAHs in this sample were measured against an external standard and were: 21 pg/m³ nitro-naphthalene, 10 pg/m³ nitro-anthracene, 77 pg/m³ nitro-fluoranthene, and 14 pg/m³ 2-nitro-pyrene.

A zoom on the elution window of nitro-fluoranthene and the nitro-pyrene isomers is shown in Figure 3A. The compounds can easily be detected. The LOD is around 1 pg, corresponding to 1 pg/m³ in air.

For comparison, the same sample was analyzed without purification on an Agilent 7890A GC system/Agilent 5975C Series GC/MSD using EI in SIM mode. The elution window for nitro-fluoranthene (t_R = 12.5 minutes) and nitro-pyrenes (t_R = 12.8 and 12.9 minutes) obtained on the single quadrupole instrument is shown in Figure 3B (extracted ion chromatograms on monitored SIM ions 247 and 201). Due to the high background, the solutes could not be detected in this case.

This example clearly illustrates how the extra dimension in detection results in a much higher specificity and selectivity, allowing the detection of target solutes at trace levels in complex matrices.

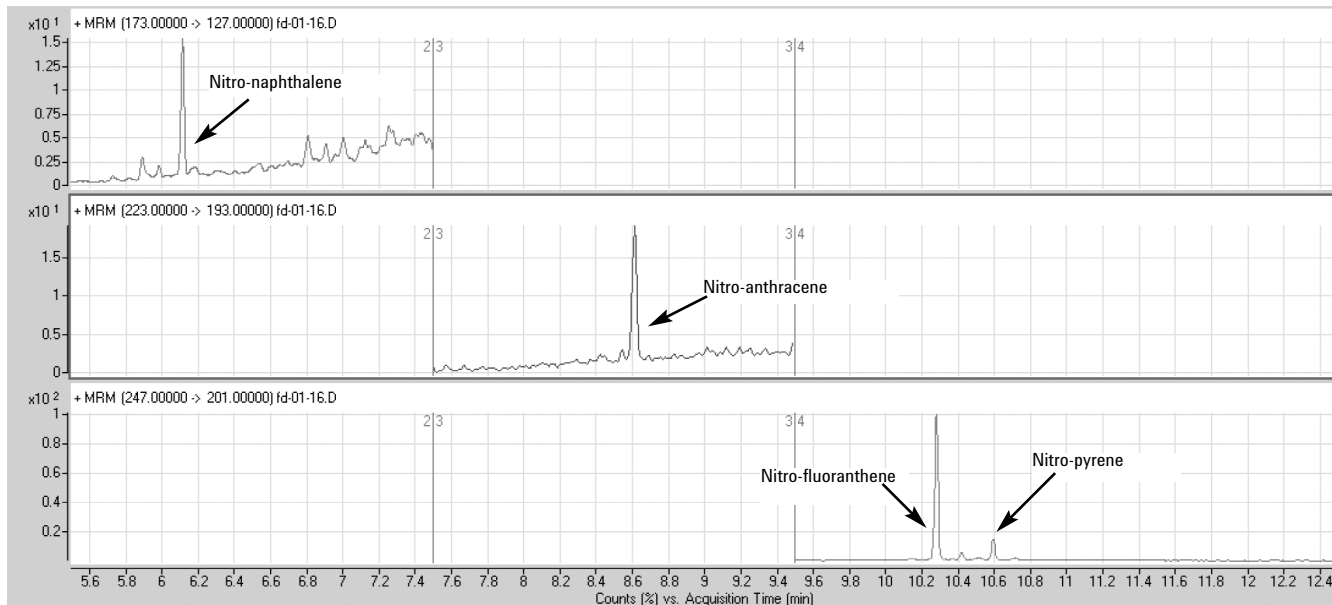
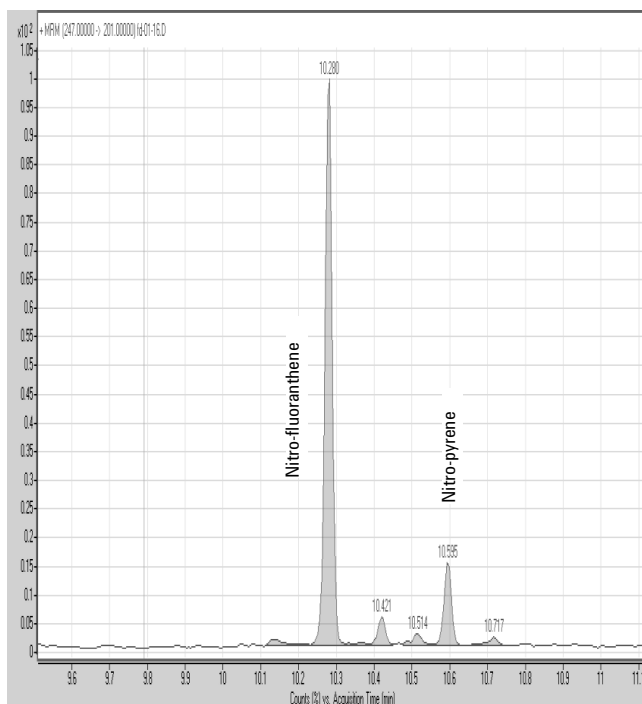
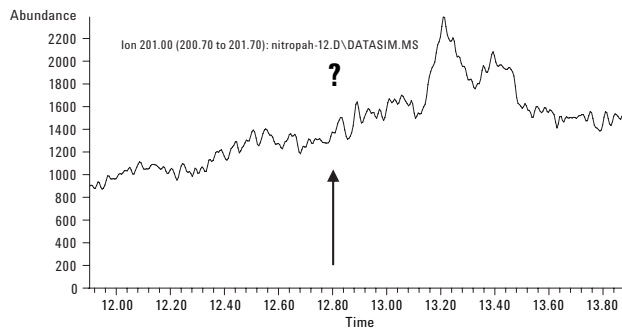
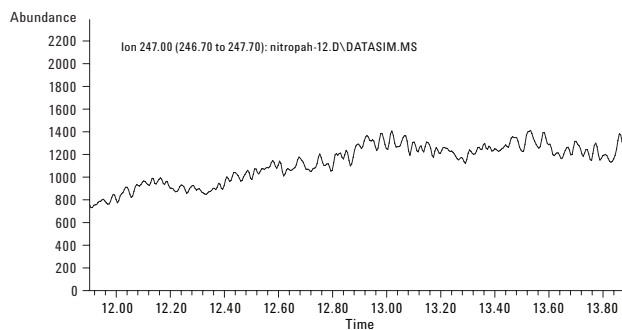


Figure 2. MRM chromatograms of nitro-PAHs in extract of urban air particulates.



3A. GC/QQQ chromatogram for nitro-fluoranthene and nitro-pyrenes.



3B. Extracted ion chromatograms over the expected retention time window for nitro-fluoranthene and nitro-pyrenes obtained by GC/MS in SIM mode.

Conclusions

Using the Agilent 7000A triple quadrupole GC/MS system, high sensitivity and extremely high selectivity were obtained for the determination of nitro-polycyclic aromatic hydrocarbons in air particulate extracts. While laborious sample preparation or a multidimensional GC is needed to detect these compounds by GC/MS in SIM mode using a single quadrupole instrument, the crude extract could be analyzed directly by GC/MS/MS in MRM mode. The solutes are selectively detected at pg/ μ L level, corresponding to pg/m³ level in air.

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