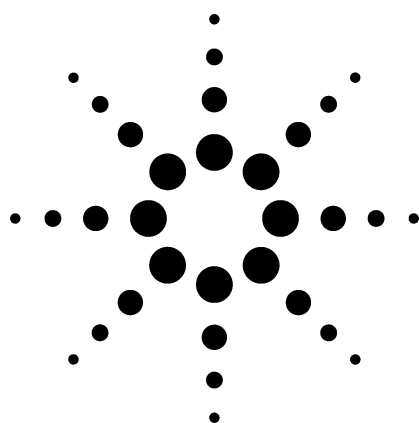


# Analysis of Nitroaromatics and Nitro-Polycyclic Aromatic Hydrocarbons by Capillary Gas Chromatography with the Agilent 6890 Micro-ECD



## Application

Gas Chromatography

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### Abstract

**A new electron capture detector (ECD) for the Agilent 6890 Series gas chromatograph (GC) allows very sensitive detection of nitroaromatic compounds at low picogram levels with a linear response over three orders of magnitude.**

**This application note describes the performance of the new 6890 Series Micro-ECD when analyzing two types of nitro-aromatic compounds—explosives and nitrated polycyclic aromatic hydrocarbons (nitro-PAHs).**

### Introduction

Electron capture detection is most often used for the sensitive and selective detection of halogenated compounds. However, other compound classes also have electron capturing properties and can, therefore, be detected at low levels using an electron capture detector (ECD). Compounds containing a nitro-function—particularly nitroaromatics—are strong electron-capturing molecules. The ECD provides a very sensitive tool for trace analysis of these solutes.

This application note demonstrates that the 6890 Series Micro-ECD provides an extremely sensitive alternative to the typical NPD or MS detection<sup>1,2</sup> for nitro-PAHs and explosives.

### Experimental

The analyses were performed on an 6890 Series GC. Injection was automated splitless using an Agilent 7673 automatic sampler. The instrument configuration and analytical conditions used for the analysis of the nitro-PAHs and explosives are summarized in table 1.

### Results and Discussion

The sensitivity of the ECD depends on the makeup flow rate. The 6890 Micro-ECD optimized the argon/5% methane (Ar/CH<sub>4</sub>) makeup gas flow rate for the analysis of nitro-PAHs. Nitro-pyrene was used as test solute. The makeup flow rate was varied from 10 to 80 mL/min; at each setting, five runs were made.

Figure 1 shows the mean peak areas plotted versus the makeup flow rate. The optimum flow rate was obtained between 20 to 30 mL/min. At lower flow rates, the peak area decreased and the detector became less stable, shown in the increasing standard deviation on peak area. At higher flow

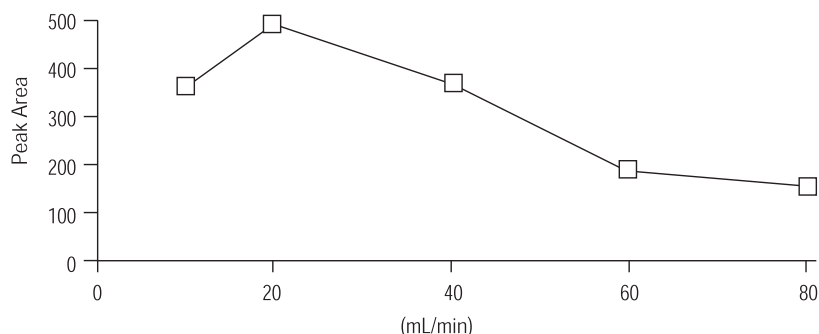


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**Table 1. Instrumental Configuration and Analytical Conditions**

<b>Chromatographic System</b>	
Gas chromatograph	6890 Series
Inlet	Split/splitless
Detector	Micro-ECD
Automatic sampler	7673 Series
Liner	Single taper deactivated (part number 5181-3316)
Data handling	ChemStation (DOS Series)
Column	30 m x 0.25 mm id x 0.25 $\mu$ m HP-5 MS (part number 19091S-433)
<b>Experimental Conditions</b>	
Inlet temperature	250 °C
Injection volume	1 $\mu$ L
Injection mode	Splitless
Purge time	0.75 min
Purge flow	50 mL/min
Carrier gas	Hydrogen
Head pressure	58 kPa at 50 °C
Carrier gas mode	Constant flow
Flow, velocity	1.4 mL/min, 40 cm/s
Oven temperature	50 °C, 1 min initial, 20 °C/min to 320 °C, 0.5 min hold
Detector temperature	320 °C
Detector gases	Argon/5% methane: 20 mL/min

**Figure 1. Peak area of 1-nitropyrene versus argon/5% methane makeup gas flow rate.**

rates, the detector was stable (exhibiting a small standard deviation), but sensitivity drastically decreased.

Nitrogen is an alternative makeup gas for electron capture detection. It can usually be used interchangeably with Ar/CH<sub>4</sub>; similar results for the effect of makeup gas flow rate are expected.

Next, the linearity of the detector response was measured. Using nitropyrene as the test solute, standard solutions of 1, 10, 50, 100 and 1,000 ppb were analyzed. The calibration curve for this compound, as shown in figure 2, exhibits a very

good correlation coefficient ( $r = 0.99996$ ).

### Nitrated Polycyclic Aromatic Hydrocarbons

Nitro-PAHs are an important class of environmental pollutants.<sup>3</sup> Polycyclic aromatic compounds are formed during incomplete combustion of organic material. In the presence of nitrogen oxides (NO<sub>x</sub>), the neutral PAHs (such as naphthalene or pyrene) are converted into nitro-PAHs.<sup>3-5</sup>

The nitro-PAHs have much higher mutagenic and carcinogenic activity

than the neutral PAHs, but their extremely low concentration (measured as pg/m<sup>3</sup>) in environmental samples, particularly air particulates, makes them difficult to monitor. Very sensitive detection is needed.

Using the optimized GC conditions, a mixture of 11 nitro-PAHs, each having a concentration of 40 pg/mL (40 ppb), was analyzed. The chromatogram for this analysis is shown in figure 3. Good peak shapes were obtained for all compounds. The detection limit, which varied from 0.1 to 1 pg for the different PAHs, is at least one order of magnitude lower than that obtained by nitrogen-phosphorus detection (NPD), mass spectrometry (MS), or MS-MS.<sup>2</sup> It can, therefore, be concluded that the 6890 Micro-ECD offers greater sensitivity for the detection of these nitro-PAHs than other methods.

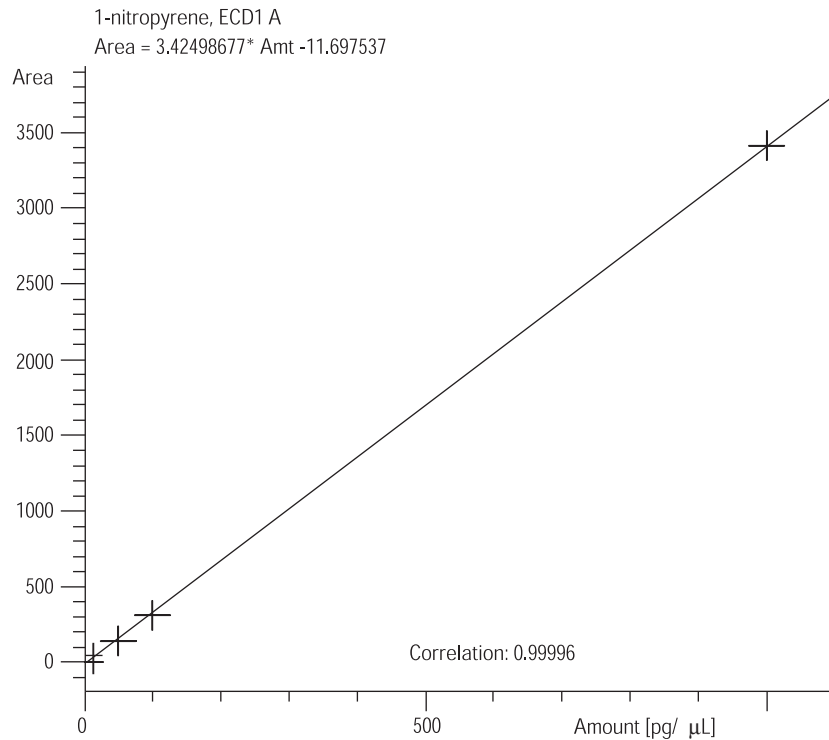
### Explosives

Explosives can be present as residues at chemical waste sites or on materials close to an explosion. Sensitive and fast methods are needed for analyzing and monitoring these compounds for environmental remediation or forensic evidence.

Although explosives are often analyzed by high pressure liquid chromatography (EPA method 8330), capillary gas chromatography (CGC) can provide a good alternative for most solutes using NPD or MS. Some of the nitro-aromatics are included in the target compound lists of EPA methods 8090 and 8270 (CGC-MS).

Explosives such as TNT (2,4,6-trinitrotoluene) contain one or more nitro-functions. CGC-ECD can provide a very sensitive and fast screening method for detecting these compounds.

The chromatogram in figure 4 shows the results of a standard mixture of explosives using the analytical conditions in table 1. The concentration of the test solutes was 100 pg/mL



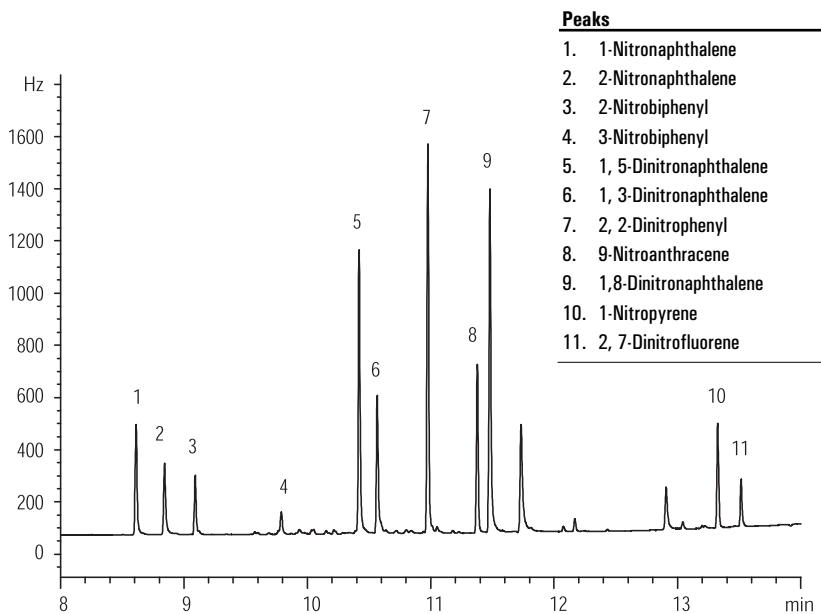
**Figure 2. Calibration curve for 1-nitropyrene from 1 to 1,000 ppb**

(100 ppb), except for 1,2-dinitrobenzene, which was present as an impurity. As the chromatogram shows, the different nitro-, dinitro-, trinitro-, and amino-nitro-compounds are well separated and elute with good peak shape.

The ECD response is dependent on the number of nitro-groups. For the mono-nitroaromatics, the detection limit is around 10 pg, while for the di- and tri-nitroaromatics the detection limit is below 1 pg. This example confirms that CGC-ECD can be used as a fast screening method for the analysis of this category of explosives.

### Conclusion

The Agilent 6890 Series Micro-ECD allows very sensitive detection of nitroaromatic compounds. The detector was successfully used for the analysis of nitrated polycyclic aromatic hydrocarbons and explosives. Detection limits below 1 pg were obtained, and the detector was found to give a linear response over three orders of magnitude.



**Figure 3. CGC-ECD analysis of nitrated polycyclic aromatic hydrocarbons (solute concentration: 40 ppb)**

Peaks	
1. Nitrobenzene	7. 1,2-Dinitrobenzene (impurity)
2. 2-Nitrotoluene	8. 2,4-Dinitrotoluene
3. 3-Nitrotoluene	9. 1,3,5-Trinitrobenzene
4. 4-Nitrotoluene	10. 2,4,6-Trinitrotoluene
5. 1,3-Dinitrobenzene	11. 4-amino-2,6-Dinitrotoluene
6. 2,6-Dinitrotoluene	12. 2-amino-4,6-Dinitrotoluene

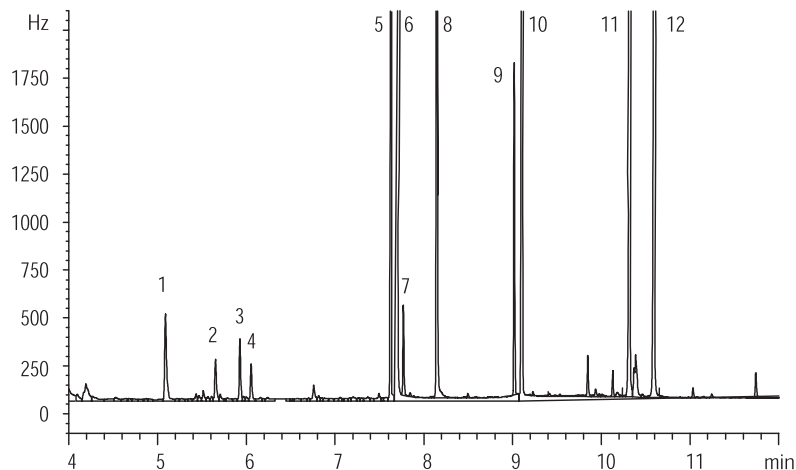


Figure 4. CGC-ECD analysis of explosives (solute concentration: 100 ppb)

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