

# Nitro-PAH and Nitroaromatic Analysis by Direct Formation of Negative Ions

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Some of the more toxic compounds found in particulate matter produced from a diesel engine are the nitrated polycyclic aromatic hydrocarbons (NPAH). These compounds generally show mutagenic and carcinogenic activities. Other nitro compounds such as drugs and explosives are analytically important. This report describes the use of a trochoidal electron monochromator for the analysis of unsubstituted PAHs and the corresponding nitro-PAHs as well as a variety of other nitro-substituted compounds including three common explosives. Isomer distinction is accomplished by using a tunable-energy electron monochromator. A surprising observation is that CID fragmentation is found to depend on the electron-capture resonance for precursor-ion formation.

A new high-current trochoidal electron monochromator<sup>1</sup> has been designed and interfaced to a JEOL AX505 magnetic-sector mass spectrometer. The electron monochromator provides a means for controlling the ionizing electron energy over the 0 eV to 30 eV range with an electron energy resolution of  $\pm 0.3$  eV and output currents in excess of 200  $\mu$ A. This permits the direct formation of negative ions without using an energy-moderating buffer gas, and it provides a means for measuring electron capture resonances and forming ions in specific energy states. The electron monochromator has demonstrated a detection limit of 10 fg of hexachlorobenzene (splitless injection) with a signal-to-noise ratio of 31:1. A linear response has been measured for octafluoronaphthalene with concentrations ranging over seven orders of magnitude. Linked-scan MS/MS and selected reaction monitoring have been used to examine energy-dependent fragmentation.

Twenty seven nitro-PAHs and nitroaromatic compounds were examined along with standard samples of unsubstituted PAHs. Although some of the low-molecular-weight unsubstituted PAH's (naphthalene, acenaphthene and fluorene) and do not show any significant ion current at electron energies near zero eV, molecular anions and the  $\text{NO}_2^-$  fragment ion were observed at this energy for all of the nitro-PAH's examined. Common fragment ions observed for the NPAHs include  $[\text{M}-\text{NO}]^-$ ,  $[\text{M}-\text{NO}_2]^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}^-$ . The highest sensitivity for the unsubstituted PAHs was observed for indeno[1,2,3-cd]pyrene, while the NPAHs showed roughly equal responses.

The use of the common  $\text{NO}_2^-$  fragment ion has been reported by Laramee and Deinzer<sup>2,3</sup> at Oregon State to distinguish explosive nitro compounds from interferences. We report that the same common fragment ion can be used to distinguish structural isomers of nitro compounds. For example, the ratios of the two electron capture resonances at  $\sim 1.2$  eV and  $\sim 3.4$  eV vary strongly for the formation of  $\text{NO}_2^-$  from the three isomeric nitrotoluenes.

Further, we report for the first time a dramatic variation in MS/MS fragmentation as the electron capture resonance energy for the precursor-ion formation is varied. MS/MS spectra were measured at two different electron energies for product ions resulting from the fragmentation of  $[\text{M}-\text{H}]^-$  from nitrobenzene. At the lower-energy resonance ( $\sim 3.5$  eV), the mass spectrum is dominated by  $[\text{M}-\text{NO}]^-$ . At an electron energy of  $\sim 6.5$  eV, the mass spectrum shows approximately equal abundances of  $[\text{M}-\text{NO}]^-$  and  $\text{NO}_2^-$ . Selected reaction monitoring of the reactions  $122 \rightarrow 92$  and  $122 \rightarrow 46$  was carried out while scanning the electron energy. The results showed a dramatic dependence of fragment-ion abundance on ionizing electron energy. In addition, the combination of SRM with electron-energy scanning provides an extremely selective method for detecting target compounds, and it may offer an additional approach to isomer discrimination. This suggests the possibility that ions formed in different electron-capture resonances may have different structures. Further experiments are underway to examine these hypotheses.

Lastly, the electron monochromator mass spectra obtained with near-zero eV electron for the three explosives TNT, RDX, and PETN were compared with published data<sup>4</sup> for the reversal electron attachment detector (READ). While similar results were obtained by both methods, the electron monochromator mass spectra show less fragmentation and show some high-mass fragments that were not reported for the READ device. This confirms the ability of the electron monochromator to produce a near-zero energy electron beam with good energy resolution.

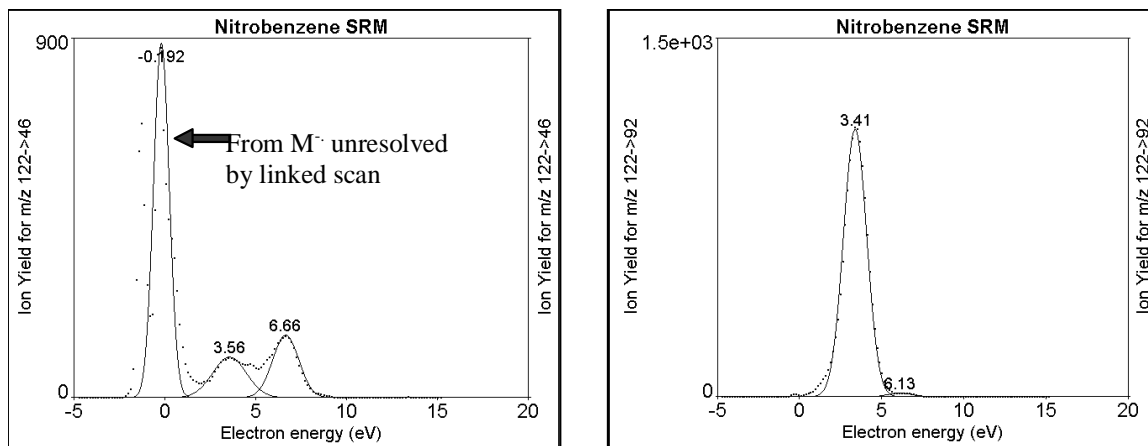


Figure 1. Selected reaction monitoring for the reactions 122->46 and 122->92 as a function of ionizing electron energy. This illustrates the dependence of CID fragmentation on the electron capture resonance in which the precursor ion was formed. The collision energy was 3 kV.

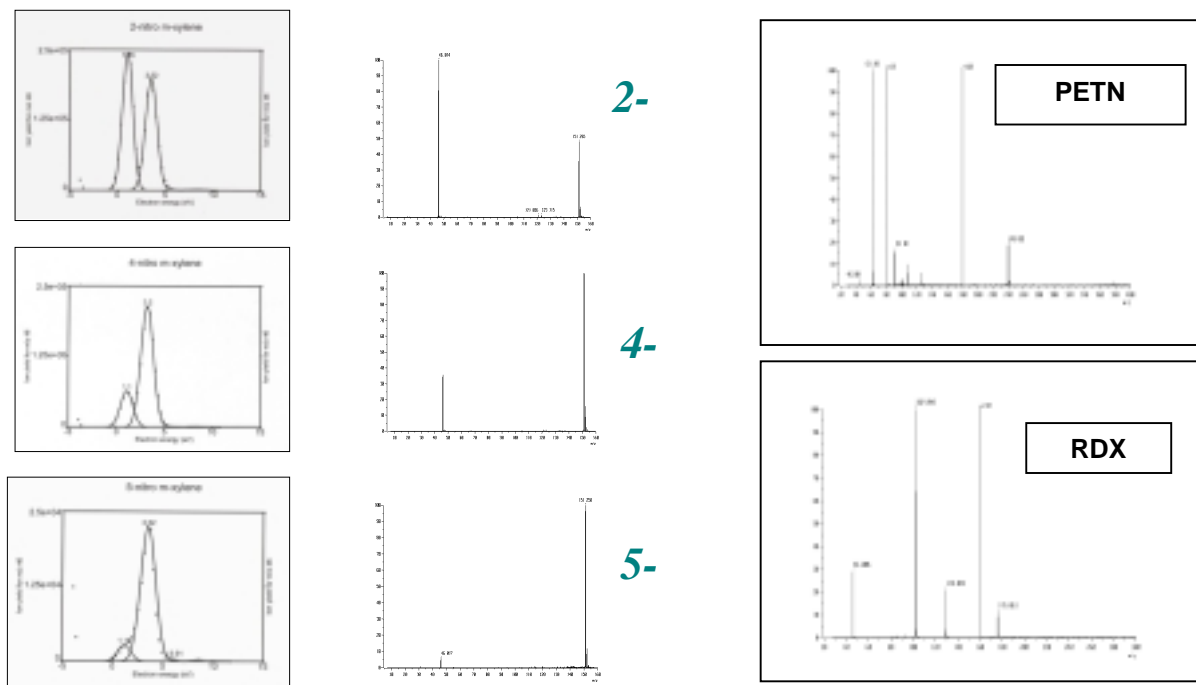


Figure 2. Mass spectra and electron-capture resonances for formation of  $\text{NO}_2^-$  from three isomers: 2-, 4-, and 5-nitro-m-xylene.

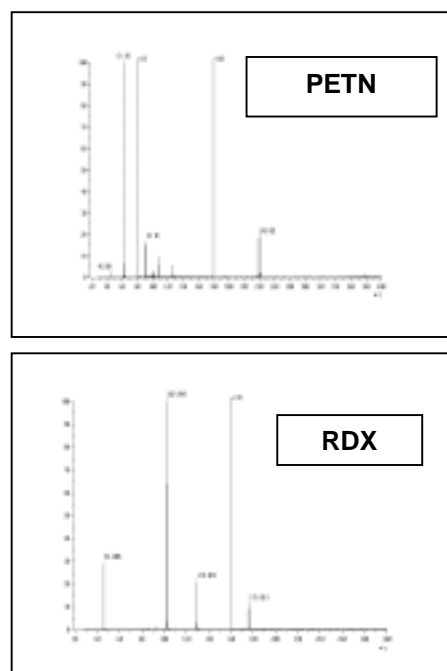


Figure 3. near-zero eV electron monochromator mass spectra of explosives.

#### References

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