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Application of Electron-Attachment Reactions to Enhance Selectivity of Electron-Capture Detector for Nitroaromatic Explosives

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reported brief reviews of the solute modulation technique [5,6].

More recently, Grimsrud has demonstrated the use of a photodetachment-modulated ECD [7–9]. In this approach, the detector cell is doped with chemicals that form complexes with specific organohalides. UV radiation provided by a Hg arc lamp was then used for dissociation of non-complexed anions. The approach was used to discriminate between simple iodinated, brominated, and chlorinated compounds [7,8]. The chemically sensitized electron-capture detector (CS-ECD) modifies the ECD selectivity by enhancing the response of chemicals with low electron-attachment affinities. The CS-ECD techniques, unlike other modified ECD techniques, do not further focus the specificity of the ECD detector but rather allow the ECD detector to respond to otherwise poor-responding compounds, actually making the ECD a less specific detector [7].

In another approach, Hanisch has reported improved chemical class specificity based on the ratios of responses between two ECDs [10,11]. The specificity was based on differences in thermal stability of analyte molecules. In this approach, a reaction chamber consisting of a gold tube at elevated temperatures (800–950°C) was placed between two ECDs. The response differences between the two detectors arose from the thermal stability of the molecules. The lower the thermal stability of the molecule, the higher was the difference in responses of the two detectors.

The objective of the present study was to enhance the ability to selectively detect nitroaromatic explosives with ECDs. This objective was met by placing

a thermal electron source between two low-volume ECDs. The thermal electron density in the reactor was adjusted to preferentially remove a class of compounds such as nitroaromatic compounds. By monitoring the responses of the two ECDs, discrimination between nitroaromatic compounds and other chemical classes was readily achieved.

2. Experimental

Experiments were carried out with a detector setup consisting of two low-volume ECDs, designated ECD-1 and ECD-2, and a thermal electron reactor (R). A schematic of the tandem ECD reactor arrangement (ECD–R–ECD) is shown in Fig. 1. Both detectors were connected to a flow-through electron-attachment reactor with 3 cm long megabore capillary. The ECD–R–ECD arrangement was mounted on top of a commercially available gas chromatograph (Model 5890 Series II, Hewlett-Packard, San Fernando, CA, USA). The analytes of interest were separated with a 12 m×0.2 mm I.D. capillary column with a 0.33- μm cross-linked methylsilicone gum stationary phase. The outlet of the column was introduced directly into ECD-1 through a bored-through 1 mm stainless-steel fitting. The fitting was welded on the stainless-steel detector body. The fitting also served as the input for the P-10 (CH_4 -Ar, 10:90) make-up gas.

To preserve chromatographic efficiency, both detectors were of low-volume design. The detector volume of each was approximately 100 μl . A 3-mCi⁶³ Ni foil served as the radiation source in each

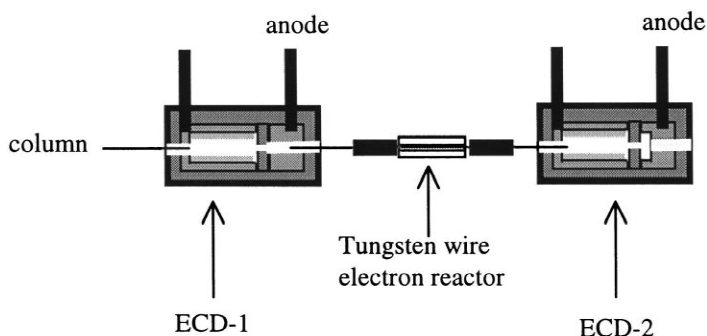


Fig. 1. Schematic of multiple ECD heated tungsten wire reactor detection.

detector. A total gas flow-rate of 15 ml min^{-1} (carrier gas+the P-10 make-up) was maintained through the detector system. The detectors were maintained at $300 \pm 0.5^\circ\text{C}$ with electronic temperature controllers (Series CN76000, Omega, Stamford, CT, USA). The response of both ECDs was monitored with two modified ECD controllers (19233-60015 Rev A, Hewlett-Packard). Modifications were necessary to obtain low reference currents.

The electron-attachment reactor consisted of a 25 mm tungsten (W) wire ($0.03 \Omega \text{ cm}^{-1}$) enclosed in a fused-silicate tube. The W wire and fused-silica tube, along with two stainless-steel inserts, were placed in a 6 mm bored-through stainless-steel union (St. Louis Valve and Fitting, St Louis, MO, USA). A close-up view of the reactor is shown in Fig. 2. Two $15 \times 6 \text{ mm O.D.} \times 1.5 \text{ mm I.D.}$ stainless-steel inserts served as the electrical connection and gas conduits. A 1.5-mm male tube fitting was silver soldered to the exterior end of the insert. The end fitting nuts were threaded orthogonal to the central capillary holes. Two posts threaded into the nuts were used for connecting a constant current power supply to the W wire, which was held in place with two set screws at the interior ends of the stainless-steel inserts. The W wire was positioned in the center of a 10-mm fused-silica tube ($1.2 \text{ mm I.D.} \times 6.35 \text{ mm O.D.}$). Polyimide ferrules were used to form a gas-tight, electrically insulated seal around the stainless-steel inserts. To minimize adsorptive losses of analytes, all stainless-steel components were treated with Silicosteel treatment (Restek, Bellefonte, PA, USA).

The test analytes were dinitrobenzene (DNB,

Eastman Kodak, Rochester, NY, USA); 2,6-dinitrotoluene (2,6-DNT, K and K Labs., Plainview, NY, USA); 2,4-dinitrotoluene (2,4-DNT, Aldrich, Milwaukee, WI, USA); 2,4,6-trinitrotoluene (TNT, Rock Mechanics Department, University of Missouri, Rolla, MO, USA); hexachlorobenzene; pentachloronitrobenzene (Aldrich, Milwaukee, WI, USA); γ -chlordane; lindane; and malathion (Environmental Solutions, NC, USA). Solvents were of optima grade and obtained from Fisher Scientific (Pittsburgh, PA, USA).

3. Results and discussion

The principal aim of the present study was to determine whether an electron-capture detection system can be assembled to elicit selective response for nitroaromatic explosives at trace concentrations. The study was based on earlier experiments conducted in our laboratory and elsewhere on the electron-attachment reaction with nitroaromatic, polychlorinated nitroaromatic, polychlorinated aromatic and polychlorinated aliphatic compounds [12,13]. These studies have shown that the abundance of high-electron-affinity products resulting from electron-attachment reactions at ambient pressures is dependent on the structure of the parent molecule. It has been observed that the polychlorinated aromatic compounds undergo successive hydrodechlorination and yield products with high electron affinities according to the reaction outlined below.

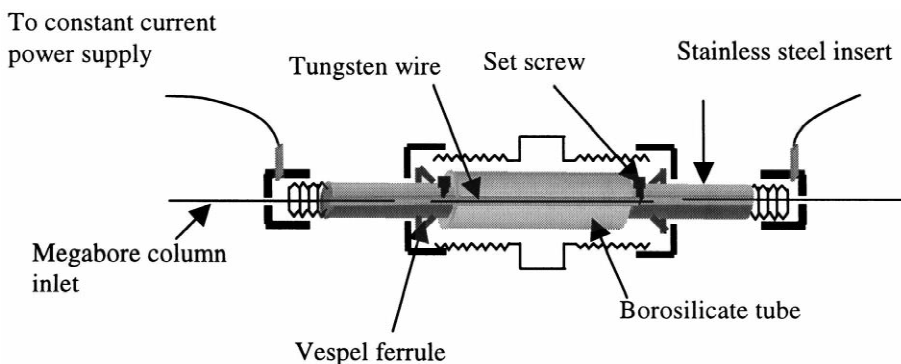
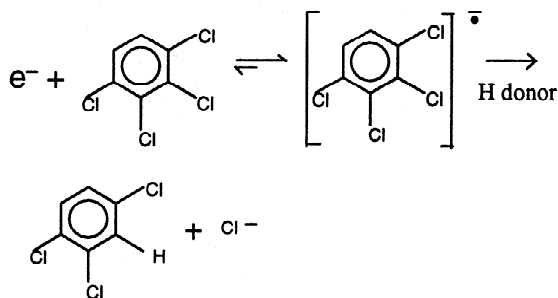


Fig. 2. Tungsten wire thermal electron reactor.



The abundance of the products is a result of resonance stabilization of the parent radical anions. Subsequent hydrodechlorination products from successive electron-attachment reactions have been reported [12]. However, the abundance of successive dechlorination reaction products is limited by a low concentration of available thermal electrons in the ECD–R–ECD arrangement. With a sufficient electron population the reaction would be limited by the decrease in electron affinity of the dechlorination product. Polychlorinated aliphatic compounds undergo similar electron-attachment initiated hydrodechlorination reactions. However, the hydrodechlorination product yields are considerably lower due to a

lack of resonance stabilization of the parent radical anion.

Unlike the polychlorinated molecules, nitroaromatic compounds do not undergo successive hydrodenitration and do not yield products with high electron affinities. In fact, no atmospheric pressure thermal electron-attachment reaction products have been reported with the loss of a single nitro group from a nitroaromatic molecule [12]. The differences in the product yields between polychlorinated and nitroaromatic compounds lead us to the design of a tandem ECD–R–ECD arrangement to distinguish nitroaromatic explosives from other molecules with high electron affinities, namely the polychlorinated organic compounds.

The response characteristics of the ECD–R–ECD system were evaluated with mixtures consisting of nitroaromatic compounds, pentachloronitrobenzene, hexachlorobenzene, γ -chlordane and lindane at varied concentrations. The responses of the two detectors were monitored under different operational modes. The results are summarized pictorially in Fig. 3. Trace a of Fig. 3 depicts the ECD-1 response for 35 μg of the nitroaromatic compounds and 8 μg of

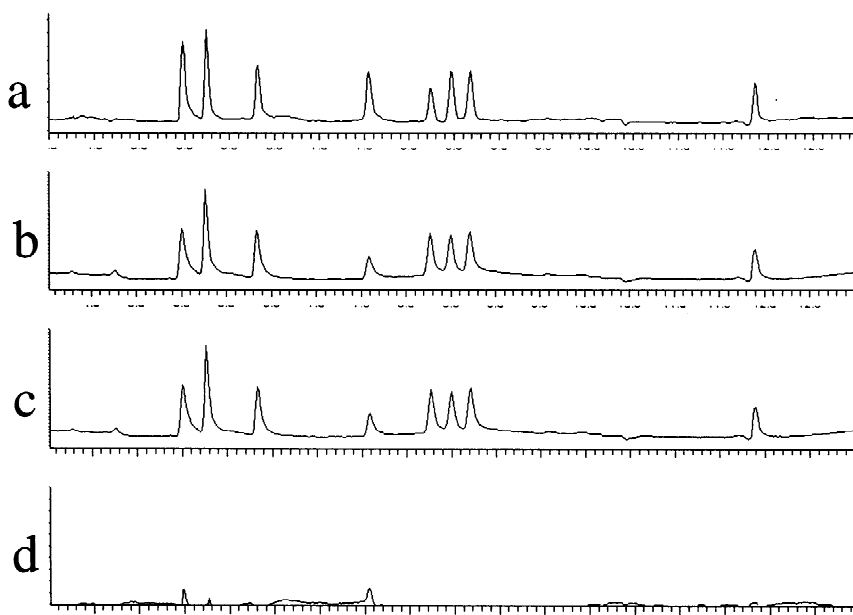


Fig. 3. Response similarity between ECD-1 and ECD-2. Chromatograms a–d of DNB, 2,6-DNT, 2,4-DNT, TNT, hexachlorobenzene, γ -chlordane, and lindane in their respective elution order. (a) ECD-1 response to test mixture, (b) ECD-2 response with ECD-1 off, (c) ECD-2 response with ECD-1 operating, (d) subtraction of ECD-2 from ECD-1.

the chlorinated analyte. Trace b represents the ECD-2 response to the same analyte mixture with no electron-attachment reactions in ECD-1 or the reactor. The electron-attachment reactions in ECD-1 were shut off by applying a -30 V d.c. potential to the foil in a manner similar to one demonstrated by Aue and Kapila [13]. The reactor was turned off, by maintaining a low tungsten wire current. Despite a slight band broadening, the overall similarity between the responses of the two detectors can be readily observed. Trace c shows the ECD-2 response again, but in this case ECD-1 was in normal operational mode. The response similarity of ECD-2 with ECD-1 off and on is self evident, indicating that a very small portion of the analyte is consumed

through the electron-attachment reactions in the first detector. Trace d shows the ECD-1 response after subtracting the ECD-2 response ($\text{ECD-1} - \text{ECD-2}$). The resulting trace is practically a straight line because of the response similarity. The results indicated that if nitroaromatic compounds, or other compounds for that matter, could be selectively removed from the gas stream during the transport from ECD-1 to ECD-2, a selective response could be obtained for these analytes.

The removal of nitroaromatic compounds from the gas stream was carried out in the electron-attachment reactor. The results of the experiments are shown in Fig. 4. Chromatograms 4a and b depict the response of the ECD-1 and ECD-2 obtained simultaneously

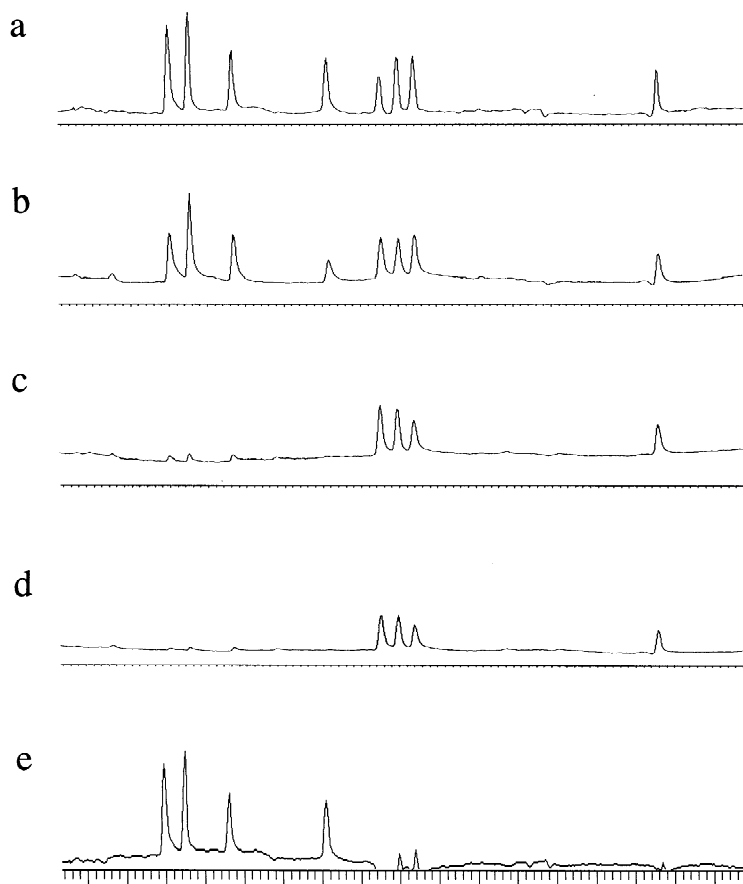


Fig. 4. Selective identification of nitroaromatic compounds. Chromatograms a–e of DNB, 2,6-DNT, 2,4-DNT, TNT, hexachlorobenzene, γ -chlordane, and lindane in their respective elution order. (a) ECD-1 response to test mixture, (b) ECD-2 response to test mixture with 2.0 A supply current to filament reactor, (c) ECD-2 with 2.78 A filament current, (d) ECD-2 with 2.85 A filament current, (e) subtraction of ECD-2 response from the ECD-1 response with a 2.85 A filament current.

from the same injection of the test analytes mentioned earlier. The reactor tungsten current during acquisition of these chromatograms was set at 2.0 A.

Chromatograms 4c and d show the response of ECD-2 for the same analytes in successive injections. The response differences resulted from changes in the reactor tungsten wire current and the associated electron emission current. Chromatograms 4b–d were obtained by varying the filament current from 2.0 to 2.85 A. It is clear that, at a filament current of 2 A, the response of ECD-2 was essentially the same as in trace 3c. An increase in the filament current to 2.78 A resulted in a dramatic decrease in the response of the nitroaromatic compounds in ECD-2, while the response of polyhalogenated molecules stayed essentially the same. A further increase in the filament current to 2.85 A resulted in a slight decrease in the ECD-2 response for polychlorinated compounds as well. The chromatogram in trace 4e shows the response of ECD-1 minus the response of ECD-2 with a reactor filament current of 2.85 A. The small change in tungsten wire current leads to a significant change in the response of the nitroaromatic compounds.

Previous work has shown conclusive evidence for the efficient formation of pentachlorobenzene from pentachloronitrobenzene through a thermal electron-attachment reaction.

The lack of change in response of the pentachloronitrobenzene from changes in reactor conditions suggests that the ECD-2 response is generated by the residual pentachloronitrobenzene and the product, pentachlorobenzene which has a similar response factor in the ECD as the parent compound. Comparing the response of ECD-1 with that of ECD-2 with the reactor at 2.85 A, it is evident that the multiple ECD arrangement can be employed to distinguish nitroaromatic compounds from polychlorinated analyte evaluated in the test mixture. The enhanced selectivity for nitroaromatic compounds can be clearly observed from subtracting ECD-2 from ECD-1 at 2.85 A shown in trace 4e. Similar selectivity was obtained against malathion, a thiophosphate pesticide that responds well in an ECD.

It is important to point out that the tungsten electron-attachment-based reactor indeed functions primarily as an electron-attachment reactor rather than a thermal reactor, which selectively destroys

explosive nitroaromatic compounds. Previous work has shown that polychlorinated nitroaromatic compounds preferentially lose the nitro moiety through the electron-attachment reaction and efficiently yield polychlorinated products [13,14]. Similar results have been obtained with a tungsten wire reactor. Furthermore, the extent of the electron-attachment reaction could be controlled by applying a positive potential to a collector electrode placed in the vicinity of the filament in a manner similar to one reported in a previous study [12,14]. The positive potential on the collector energizes and removes thermal electrons, making them unavailable for electron-attachment reactions. This hypothesis is supported by determining the change in filament resistance due to changes in filament temperature at different filament currents. Temperature changes were estimated using Eq. (1):

$$RT_2 = RT_1[1 + \alpha(T_2 - T_1)] \quad (1)$$

where R is resistance (Ω), T is temperature ($^{\circ}\text{C}$), and α is $4.5 \cdot 10^{-3}$ for tungsten at 20°C . The calculated temperature increases from a non-emission current to an emission current is 35°C . In addition, if the tungsten wire is oxidized the reactor does not selectively remove the nitroaromatic explosives even at much hotter tungsten wire temperatures corresponding to a filament current of 4.5 A. It was observed that at filament currents above 4.5 A, the hot oxidized tungsten wire destroys all of the test analytes without any apparent discrimination.

The extent of reaction and product formation was examined at different concentrations as shown in Fig. 5. It was observed that an order of magnitude increase in the analyte concentration did not significantly alter the extent of reaction. This was particularly true in the case of nitroaromatic molecules; e.g., an increase in amount introduced from 25 to 220 pg did not result in measurable residual analyte. This observation can be attributed to the large excess of electrons available in the present reactor. The electron:molecule ratio at the lower and higher concentrations remained well above the coulometric limits for these and other analytes examined during the study. The results tend to show that concentration of residual analyte and products obtained from electron-attachment at high

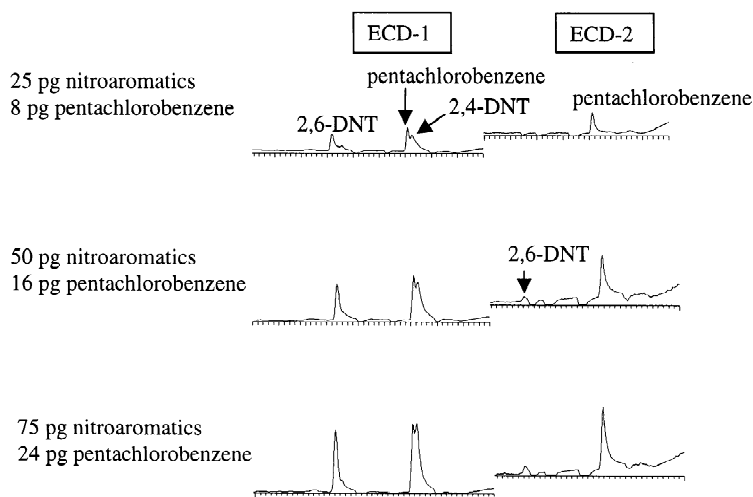


Fig. 5. The extent of reaction and product formation examined at increasing concentrations of analyte.

electron concentrations is related to the nature of the analyte molecules rather than to their concentrations.

4. Conclusion

The multiple ECD tungsten reactor detection method can improve ECD specificity. The electron-attachment reactor provides discrimination between nitroaromatic compounds and representatives of several classes of compounds. The low volume arrangement preserves chromatographic efficiency and suitable sensitivities.

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