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# TRACE ANALYSIS FOR ORGANIC NITRO COMPOUNDS BY GAS CHROMATOGRAPHY–ELECTRON-CAPTURE/PHOTOIONIZATION DETECTION METHODS

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## SUMMARY

Combined detectors in gas chromatography (GC), such as electron-capture (ECD) and photoionization detectors (PID) have been utilized for improved identification of a wide variety of organic nitro compounds. GC retention times together with relative response factors and ratios of ECD/PID response factors are reported. Detection limits with the ECD and PID, relative response factors and ratios of relative response factors were derived from results for mixtures of organic nitro compounds separated by GC with temperature programming. A new type of GC packing material, covalently bonded Permabond supports, was utilized for most of these studies.

## INTRODUCTION

Organic nitro derivatives are of analytical and toxicological interest for many reasons. Many aliphatic and aromatic nitro compounds have been found to different extents in various environmental, industrial, biological and chemical samples. Sometimes these compounds are formed within such samples from suitable precursors, and sometimes they are initially present as contaminants from other sources[1–8]. It has also become of considerable concern that many nitro compounds, especially polyaromatic derivatives, display varying degrees of mutagenicity and/or carcinogenicity[9–17]. Many nitro compounds are used as drugs, veterinary products, cosmetic ingredients, perfumes and fragrances, explosives and propellants, agricultural chemicals, industrial raw materials and intermediates, bactericides and other consumer/industrial products. Because of their wide chemical diversity and widespread distribution via consumer and industrial products, and because many are formed environmentally, many nitro compounds have become widespread environmental pollutants. There has therefore developed an intense interest in the development of trace methods of analysis and speciation for various nitro derivatives, including the use of gas chromatography (GC) with a variety of detectors, high-performance liquid chromatography

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(HPLC) with assorted detectors, as well as direct analysis via mass spectrometry (MS) and related instrumental techniques[1–8,18–22]. In the past, most trace analyses for nitro compounds present in complex sample matrices involved the use of GC with a variety of selective and/or general detection methods, such as flame-ionization detection (FID), electron-capture detection (ECD), alkali flame-ionization detection (AFID), thermal energy analysis (TEA) and Coulson electrolytic conductivity detection (CECD). Within the past few years, many HPLC-based analyses for nitro compounds have been described, making use of electrochemical detection, ECD, photoconductivity detection, TEA and others[8,23–26].

Most trace analyses for organic nitro compounds still rely on GC detector methods, partly because of the lower detection limits possible and the widespread availability of the instrumentation required. Recently there has been a distinct interest in the application of photoionization detection (PID) for a wide variety of trace organic analyses. At the same time, there is considerable interest in combining the PID with other selective and/or general GC detectors for improved analyte identification in trace analysis[27–34]. The use of more than one detector response per analyte of interest has recently gained widespread popularity and acceptance as a valid analytical method for improving the identification of individual GC analytes[21,31–33,35–42]. In most applications, the combination of a general and a selective or of a selective and a selective detector for organic nitro compounds should provide more compound specificity and better identification than the use of two detectors that respond to about the same extent with such materials. Thus, the use of an FID with an ECD for nitro compounds would not be expected to provide any unusual degree of analyte specificity, because most aliphatic or aromatic nitro compounds would provide about the same degree of response on each detector. On the other hand, a combination of an FID with a PID or of an ECD with a PID, or all three simultaneously, should provide an unusual degree of compound identification and specificity. This assumes, of course, that the PID will indeed demonstrate more selectivity for aliphatic *versus* aromatic nitro derivatives than either the FID or the ECD. This assumption has been supported by earlier work of Driscoll *et al.*[28]. With regard to the application of the PID to nitro derivatives in general, this has been described for a very limited number and variety of such compounds by Langhorst[22], who reported the PID relative responses *versus* benzene for nitrobenzene, 2,4-dinitrobenzene, 4-nitrophenol and 2,4-dinitrophenol, but did not mention any aliphatic nitro derivatives.

We describe here the simultaneous application of both the ECD and the PID to a large number of aliphatic and aromatic nitro derivatives, including nitropentane, nitrocyclohexane, *o*-, *m*- and *p*-nitrotoluene, 2,3-, 2,4-, 2,6- and 3,4-dinitrotoluene, *o*-, *m*- and *p*-dinitrobenzene, polycyclic aromatic hydrocarbons and their mono-nitro derivatives (PAHs and nitro-PAHs). PAHs and nitro-PAHs are of considerable interest as air and water pollutants, and because of their demonstrated carcinogenicity and/or mutagenicity in mammalian systems. All of these GC–ECD/PID analyses were performed with either Ultrabond 20M, Permabond Methylsilicone and/or Permabond PEG 20M packing materials in glass packed columns. Permabond packing materials have recently gained widespread attention because of their very light loading, covalent attachment of the organic stationary phase to the solid, inert support and their general high temperature stability[34]. We describe here the GC separation

conditions utilized, detector operating parameters, retention times and resolution factors, detection limits with the ECD/PID, linearity ranges of response, normalized response factors on various detectors and related analytical parameters of interest for these nitro derivatives. All of this work has thus far involved the use of commercially available chemical standards, but the final analytical and detection methods and results should be directly applicable to real samples for the same or other nitro derivatives. It is the intention of this work that such methods will indeed be eventually applied in other laboratories to practical environmental, industrial, biological and toxicological samples.

## EXPERIMENTAL

### *Equipment*

A Varian Model 3700 gas chromatograph (Varian, Palo Alto, CA, U.S.A.), equipped with conventional Varian FID and ECD detectors, was used. A separate PID unit (Model P1-51-01, HNU Systems, Newton, MA, U.S.A.) was mounted external to the main GC oven, on top of the GC itself, with external heating tape applied to the interface, in order to prevent any condensation of the GC effluents after their exit from the column oven. For dual detection in parallel (ECD/PID), it was necessary to construct a special, glass-lined, metal tee splitter using 1/6 in. × 0.5 mm I.D. glass-lined stainless-steel tubing (Scientific Glass Engineering, Austin, TX, U.S.A.). Additional parts for this all glass-lined interface between the end of the GC column and the two detectors included drilled-through Swagelok 1/8 × 1/16 in. reducing unions (Cambridge Valve & Fitting, Billerica, MA, U.S.A.), and Varian detector inlets. A Weller Mini-Shop variable-speed cutter with a diamond cutting wheel (Jensen Tools, Tempe, AZ, U.S.A.) was used to cut the glass-lined metal tubing. This fixed-ratio splitter was monitored before, during and after various days' analyses, to ensure that the actual eluent split to each detector was reproducible and well defined. Temperature programming does not change the eluent splitting ratio using this type of a fixed-ratio GC splitter.

For those studies involving only nitropentane, nitrocyclohexane, *o*-nitrotoluene and 2,6-dinitrotoluene in the analyte mixture, a GC column packing of Ultrabond 20M (RFR Corp., Hope, RI, U.S.A.) was used, in a packed glass column (6 ft. × 2.0 mm I.D.). All of the aromatic nitro derivatives, PAHs and nitro-PAHs were eventually analyzed on two separate GC columns with slightly different temperature programming conditions. The first such column was a glass packed column (6 ft. × 2.0 mm I.D.) of Permabond methylsilicone (HNU Systems) and the second was a glass packed column (6 ft. × 2.0 mm I.D.) of Permabond PEG 20M (HNU Systems). Specific GC separation conditions for each of these columns are indicated under Results and Discussion. The support gases used for the GC carrier gas and detector support gases (FID) were obtained from Matheson Gas Products (East Rutherford, NJ, U.S.A.). All GC detector chromatograms were recorded on a Linear dual pen recorder (Linear Instruments, Irvine, CA, U.S.A.) at a chart speed of 1 cm/min and an output of 1 mV.

### *Reagents and solvents*

Individual nitro compounds, PAHs and nitro-PAHs were obtained from a

variety of commercial sources, including Pfaltz & Bauer (Stamford, CT, U.S.A.), Aldrich (Milwaukee, WI, U.S.A.), Chem Service (West Chester, PA, U.S.A.), MCB Chemicals (Medford, MA, U.S.A.) and Fisher Scientific (Fair Lawn, NJ, U.S.A.). All of the solvents used to prepare the standard solutions for GC analyses were of HPLC grade, distilled-in-glass, and were obtained from commercial suppliers, such as J. T. Baker (Phillipsburg, NJ, U.S.A.) and MCB Omnisolv (Doe & Ingalls, Medford, MA, U.S.A.). Chemicals and solvents were used as received.

*Methods*

Individual stock solutions of each nitro derivative and mixtures of nitro compounds, PAHs and nitro-PAHs were prepared in volumetric flasks by carefully weighing or measuring out an initial amount of each standard. The solvents used to dissolve such standards were chosen so that they would be compatible with the particular GC detectors being used. In most instances, acetone alone or hexane–acetone (1:1) was satisfactory. The solutions were kept in the dark in a refrigerator, and if a question arose with regard to changes in concentration levels, then fresh standard solutions were prepared on the same day as the analytical studies involved. All standard solutions were prepared with an internal standard, *o*-nitrotoluene, added at the same time as the compounds of interest. Injections (generally less than 2 $\mu$l) on to the GC column were made with a Hamilton Model 701N syringe (Hamilton, Reno, NV, U.S.A.). Solvent blanks were always injected before and after the standard solutions of analytes, to ensure that any peaks being observed were not derived from the solvent itself or any impurities therein. All injections of standards and solvent blanks were performed at least in duplicate, under identical GC–detector operating conditions.

## RESULTS AND DISCUSSION

All of the results were obtained using packed glass columns, mostly with Permabond-type packing materials, and in most instances using temperature programming. Capillary columns have always been an alternative approach, but this would have required the use of modified detectors, in order to utilize fully the efficiencies inherent within capillary-type columns. We have not found it necessary to utilize capillary columns for these studies, as improved analyte specificity has been achieved with conventional packed columns together with different selectivities inherent in ECD and PID methods. Combined detector responses, normalized relative response factors (RRFs) and ratios of such relative response factors (ECD/PID) have provided greatly improved selectivity over single detector methods in conventional GC. For unusually complex sample mixtures, capillary column resolutions may prove a necessity, but this would require suitable modifications to the dimensions of the conventional GC detectors employed.

In all of the PID analyses, a 10.2 eV lamp was used, partly because of its greater light intensity at this power level. As other lamps of higher and lower power are commercially available, it should be possible in future work to obtain additional selectivity differences for the same nitro derivatives or PAHs. Such data, together with the ECD responses described below, would then provide additional analyte identification and selectivity.

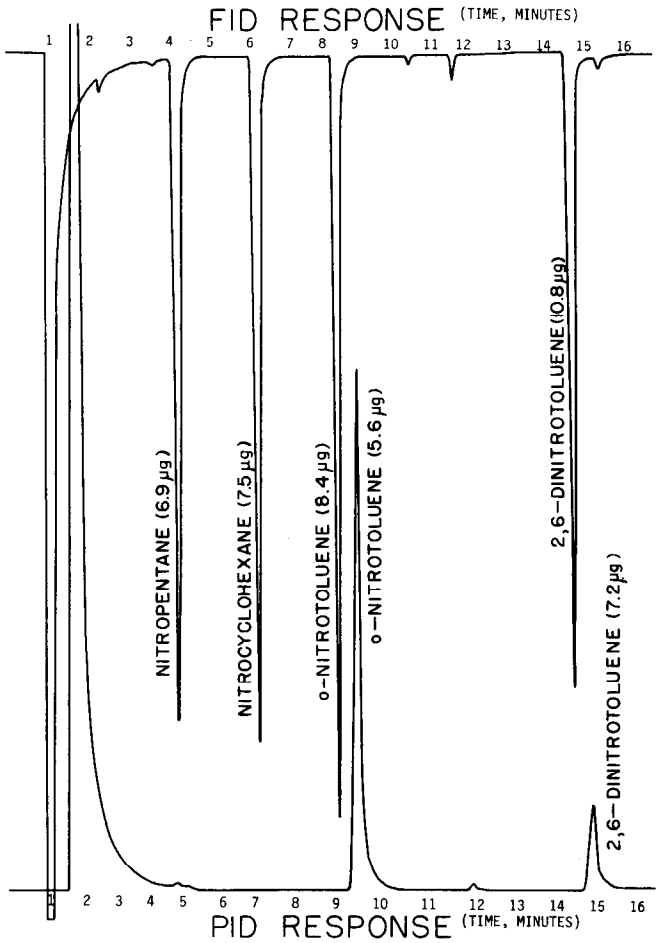


Fig. 1. GC–FID/PID chromatograms of four standard nitro organics using a 6 ft × 2.0 mm I.D. glass column of Ultrabond 20M, with temperature programming from 50°C (2 min) to 180°C at 10°C/min, with a final hold at 180°C. Injector and detector temperatures, 230–250°C. Carrier gas (nitrogen) flow-rate, *ca.* 40 ml/min, split 70:30 between FID and PID. Amounts indicated are those reaching the detector. *o*-Nitrotoluene.

We have compared the selectivity possible for equimolar amounts of four typical organic nitro compounds, *viz.*, nitropentane, nitrocyclohexane, *o*-nitrotoluene and 2,6-dinitrotoluene, using FID, ECD and PID. Fig. 1 illustrates the GC–FID/PID chromatograms for these four standards, with the amounts of each reaching the detectors as indicated. As expected, the FID responses are approximately equal for equimolar amounts of organic nitro compounds on a general-type detector. However, the PID responses are vastly different, especially when comparing aliphatic with aromatic nitro compounds. Even at the low microgram per compound levels injected here, neither of the aliphatic nitro derivatives appears on the PID trace. The differences in sensitivities for organic nitro compounds must be due to inherent differences in the ionization potentials of these compounds, as this is the physical basis for the selectivities possible with the PID. The absolute amounts of each compound

TABLE I

MINIMUM DETECTION LIMITS FOR FOUR NITRO COMPOUNDS USING THREE GC DETECTORS

GC conditions as described in Fig. 1 and text.

| *Compound* | *Detection limit (ng)* | | |
|---|---|---|---|
| | *FID* | *PID* | *ECD* |
| Nitropentane | 1.06 | 0.00* | 0.14 |
| Nitrocyclohexane | 1.04 | 0.00* | 0.03 |
| *o*-Nitrotoluene | 0.93 | 0.40 | 0.03 |
| 2,6-Dinitrotoluene | 1.13 | 2.80 | 0.01 |

* 0.00 indicates that there was no apparent PID response for these compounds at any level below 1 μg injected on-column.

reaching the PID are in the 5–10 μg range. The GC–ECD analysis for the same four organic nitro compounds, as expected, showed approximately equal responses for the mononitro materials for equimolar amounts reaching the ECD, and about double the response for the 2,6-dinitrotoluene isomer. Thus, of the three detectors initially studied here, only the PID shows a high degree of selectivity for aliphatic and aromatic nitro derivatives.

The minimum detection limits (MDLs) for these four nitro compounds, and thus indirectly the relative response factors (RRFs), are presented in Table I. The MDLs were determined using a signal-to-noise ratio of approximately 2:1 with lower and lower amounts of each nitro compound being injected and detected. As initially suggested in Fig. 1, the MDLs obtained with the FID and ECD are approximately equal within each detector category. However, the PID MDLs are vastly different from one another.

*Separations of nitro derivatives on Permabond packing materials*

Fig. 2 shows a set of GC–ECD/PID chromatograms for *o*-, *m*- and *p*-nitrotoluene, together with the specific GC–detector operating conditions. The amounts indicated are those going to each detector, taking into account the known/determined splitting ratio of the GC effluent before the detectors. Knowing the absolute splitting ratio throughout the temperature-programmed analysis, the absolute amounts of each compound injected and the determined peak heights at each recorder/detector attenuation setting, it was possible to calculate the relative response factors for individual compounds. We have taken *o*-nitrotoluene as the internal reference compound, and all other ECD and PID responses are then referenced to *o*-nitrotoluene as 1.00 on each detector. Thus, relative response factors (RRFs) are determined directly by measuring peak heights and absolute amounts of each compound reaching that detector. The ratio of peak heights (mm/cm) divided by the amount in nanograms or micrograms reaching the detector then provides normalized response factors. Normalized relative response factors are simply obtained by using the relative response factor for *o*-nitrotoluene as 1.00 and referencing all other RRFs to that value. Naturally, such calculations are based on detector responses measured or corrected at the same attenuation settings on the detector amplifier and recorder.

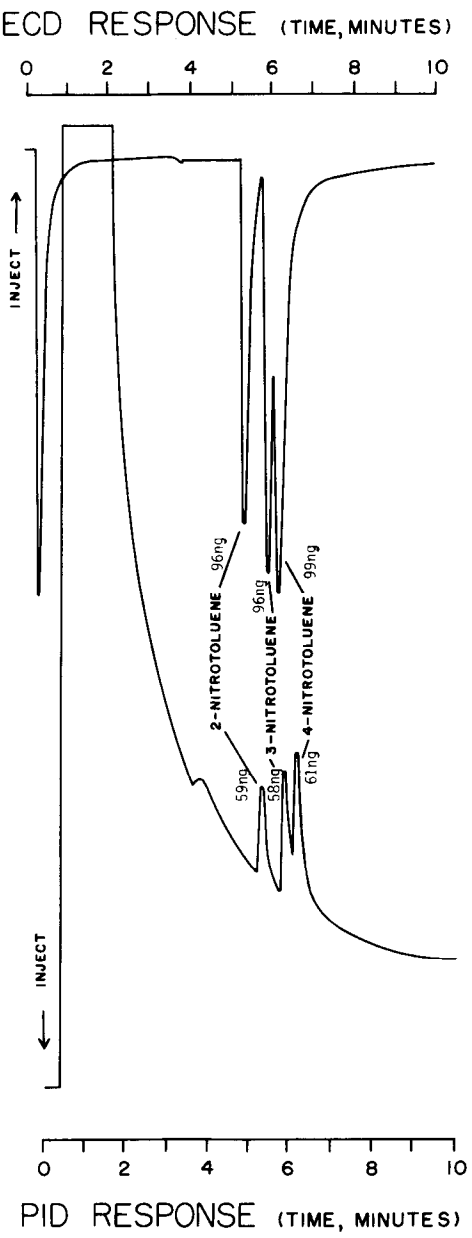


Fig. 2. GC–ECD/PID chromatograms of three mononitrotoluene isomers using a 6 ft. × 2.0 mm I.D. glass column of Permabond methylsilicone operated from 50 to 180°C with temperature programming at 10°C/min. Nitrogen carrier gas flow-rate, 30–40 ml/min, with splitting ratio 40:60 between PID and ECD. Amounts indicated are those reaching the detector.

TABLE II

RELATIVE RESPONSE FACTORS FOR NITRO AROMATICS WITH GC–ECD/PID

Data were obtained using GC conditions as in Fig. 2. The amount of each compound reaching the detector was determined knowing the amount injected with splitting ratios determined in each day's run.

| *Compound* | *Relative response factors (RRFs)** | | |
|---|---|---|---|
| | *PID* | *ECD* | *ECD/PID* |
| *o*-Nitrotoluene | 1.00 | 1.00 | 1.00 |
| *m*-Nitrotoluene | 1.06 | 1.11 | 1.05 |
| *p*-Nitrotoluene | 1.56 | 1.06 | 0.68 |
| 2,3-Dinitrotoluene | $2.92 \cdot 10^{-2}$ | 5.44 | 186.3 |
| 2,4-Dinitrotoluene | $9.00 \cdot 10^{-2}$ | 4.86 | 540 |
| 2,6-Dinitrotoluene | $2.46 \cdot 10^{-2}$ | 5.47 | 222.4 |
| 3,4-Dinitrotoluene | $1.78 \cdot 10^{-2}$ | 4.94 | 277.5 |
| *o*-Dinitrobenzene | –** | 4.86 | –** |
| *m*-Dinitrobenzene | –** | 3.31 | –** |
| *p*-Dinitrobenzene | –** | 5.81 | –** |

* Relative response factors (RRFs) were obtained by measuring peak heights (cm) and dividing by the absolute amount reaching the detector (ng/μg). *o*-Nitrotoluene was assigned an arbitrary value of 1.00 cm/ng, and other RRFs were calculated relative to *o*-nitrotoluene.

** There was no measurable PID response below μg amounts for the dinitrobenzenes.

TABLE III

MINIMUM DETECTION LIMITS FOR ISOMERIC NITRO COMPOUNDS WITH GC–ECD/PID

GC conditions as indicated in Fig. 2 and 3. Detection limits determined by using lower and lower absolute amounts of each compound injected with a signal-to-noise ratio of 2:1 at the lowest attenuation settings possible.

| *Compound* | *Detection limit (ng)* | |
|---|---|---|
| | *ECD* | *PID* |
| *o*-Nitrotoluene | 0.022 | 5.95 |
| *m*-Nitrotoluene | 0.020 | 5.61 |
| *p*-Nitrotoluene | 0.021 | 3.81 |
| 2,3-Dinitrotoluene | 0.003 | 50 |
| 2,4-Dinitrotoluene | 0.003 | 162 |
| 2,6-Dinitrotoluene | 0.003 | 59 |
| 3,4-Dinitrotoluene | 0.003 | 82 |
| *o*-Dinitrobenzene | 0.045 | –* |
| *m*-Dinitrobenzene | 0.066 | –* |
| *p*-Dinitrobenzene | 0.046 | –* |

* Indicates no apparent PID response for such compounds at any level below μg amounts injected on-column.

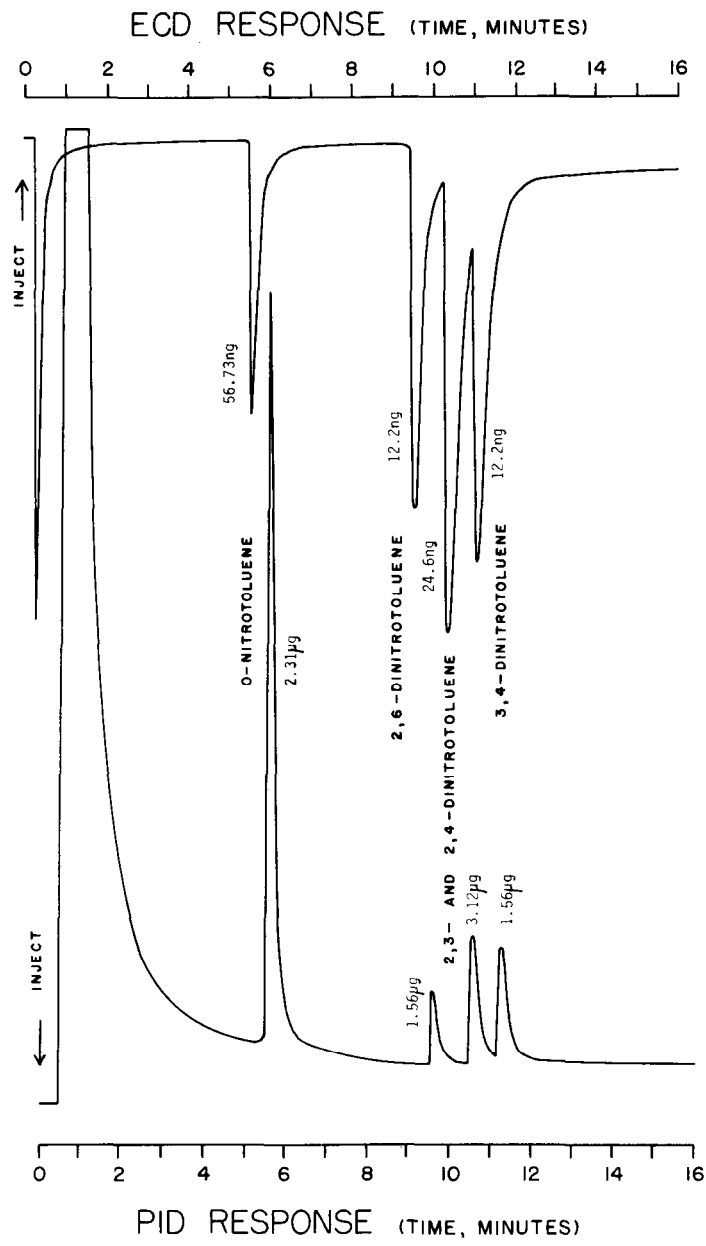


Fig. 3. GC–ECD and GC–PID chromatograms for a mixture of *o*-nitrotoluene and three dinitrotoluene isomers. Individual gas chromatograms were obtained separately and superimposed for ease of comparison of detector responses. GC conditions: 6 ft. × 2.0 mm I.D. glass column of Permabond methylsilicone at 50–180°C with programming at 10°C/min; nitrogen carrier gas flow-rate, 40 ml/min; eluent splitting ratio 40:60 (PID/ECD). Amounts indicated are those reaching the detector.

Table II summarizes the RRFs on the ECD and PID for the mononitrotoluenes, and a variety of dinitrotoluene and dinitrobenzene isomers, as described further below. For these two detectors, the RRFs within each group of aromatic nitro derivatives are about the same, and therefore the ratio of RRFs for the ECD/PID are also about the same for each group. Thus, for similar aromatic nitro isomers, neither the PID nor the ECD provides greatly improved selectivity over the FID. However, Table II indicates that when one compares the ratios of RRFs for the ECD/PID between these three classes of aromatic nitro derivatives, this does offer a unique means of characterizing each separate class. Thus, the mononitrotoluenes are clearly distinguishable from the dinitrobenzenes, as the latter do not show any response on the PID at these levels. Their ECD/PID ratios of RRFs for the dinitrotoluenes are again different from those for the other two groups of nitro aromatics in Table II.

For the GC–ECD/PID analyses of all other groups of nitro aromatics, PAHs and nitro-PAHs, we utilized *o*-nitrotoluene as an internal standard. Fig. 3 is a superimposed combination of two separately obtained chromatograms, both being obtained under identical GC conditions. Because the ECD and PID detector responses to the dinitrotoluene isomers were so very different, it was not possible, with the fixed-ratio splitter used, to obtain both ECD and PID chromatograms by a single injection of these compounds. With a variable-ratio splitter this problem could have been

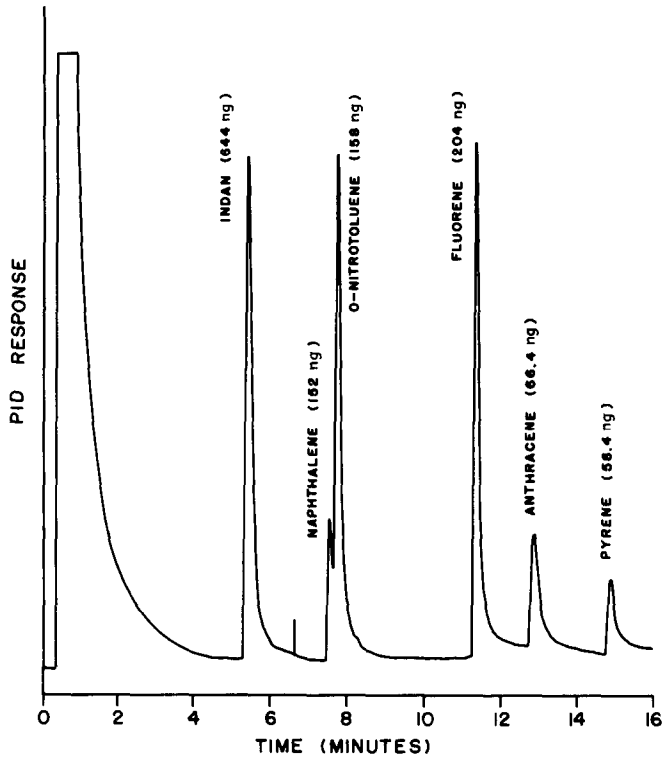


Fig. 4. GC–PID chromatogram of a mixture of PAHs with *o*-nitrotoluene. GC conditions: 6 ft. × 2.0 mm I.D. glass column of Permabond methylsilicone operated at 40–225°C with programming at 15°C/min; nitrogen carrier gas flow-rate, 15 ml/min to PID.

overcome and both chromatograms would have been obtained by a single injection. However, variable-ratio splitters do not provide fixed splitting factors, at a given setting, throughout a temperature-programmed GC analysis. In Fig. 3 there is a single peak for both 2,3- and 2,4-dinitrotoluene derivatives, which were not successfully resolved on the packing material used. However, relative response factors were obtained by separate injections of each of these two isomers, together with the internal standard, *o*-nitrotoluene. An improved resolution of all four dinitrotoluene isomers was eventually obtained with another packing material, as described below. The individual RRFs and ratios of ECD/PID RRFs for these four dinitrotoluenes are given in Table II, and these have been already compared and discussed (see above).

The minimum detection limits for the mononitrotoluenes, dinitrotoluenes and dinitrobenzenes, on both the ECD and the PID using GC conditions as given in Figs. 2 and 3, are given in Table III. In each instance, the MDLs obtained with the ECD are orders of magnitude lower than those with the PID. It is generally recognized that for organic nitro compounds, the detection limits will always be lower on the ECD than on the PID. However, compound identification and detector selectivity will generally be better with the PID than the ECD. In deciding which detector is the most useful for organic nitro compound analysis, one must first decide whether it is detectability or selectivity that is of greater concern.

The Permabond methylsilicone packing material has also been utilized for the resolution and detection with the ECD/PID of several typical PAHs and nitro-PAHs. Fig. 4 is a GC–PID chromatogram of five PAHs together with *o*-nitrotoluene as the internal standard, with the amounts going to the PID indicated. Although naphthalene is not baseline resolved from *o*-nitrotoluene, the relative peak heights can be accurately determined, together with relative response factors for all of the PAHs

TABLE IV

RELATIVE RESPONSE FACTORS (RRF) AND ECD/PID RATIOS FOR PAHs AND THEIR NITRO-PAH ANALOGS

GC conditions as indicated in Fig. 4.

| *Compound* | *ECD* | *PID* | *ECD/PID** |
|---|---|---|---|
| *o*-Nitrotoluene | 1.00 | 1.00 | 1.00 |
| Indan | $7.18 \cdot 10^{-5}$ | 0.54 | $1.34 \cdot 10^{-4}$ |
| 5-Nitroindan | 2.32 | 1.18 | 1.97 |
| Naphthalene | $8.01 \cdot 10^{-6}$ | 0.286 | $2.80 \cdot 10^{-5}$ |
| 2-Nitronaphthalene | 4.73 | 1.25 | 3.78 |
| Fluorene | –** | 0.762 | –** |
| 2-Nitrofluorene | 3.48 | 0.75 | 4.64 |
| Anthracene | $6.73 \cdot 10^{-3}$ | 0.520 | $8.83 \cdot 10^{-3}$ |
| 9-Nitroanthracene | 2.50 | 1.38 | 1.81 |
| Pyrene | $1.53 \cdot 10^{-2}$ | 0.388 | $3.94 \cdot 10^{-2}$ |
| 3-Nitropyrene | 2.18 | 0.370 | 5.89 |

* All calculations were made using peak heights and not peak areas. ECD and PID responses were first normalized to that of *o*-nitrotoluene as 1.00 (cm/ng) knowing amounts injected, detector attenuations and peak heights obtained. Analyzed as mixtures of PAHs or nitro-PAHs with *o*-nitrotoluene present.

** Not possible to obtain ECD response for fluorene at μg levels or above.

involved. Such results were further confirmed by utilizing each PAH injected separately with the internal standard. As expected, PAHs respond considerably better on the PID than on the ECD, and these relative response factors are summarized in Table IV.

Fig. 5 is a combination of two superimposed GC–ECD and GC–PID chromatograms for a mixture of five different nitro-PAHs with *o*-nitrotoluene as the internal

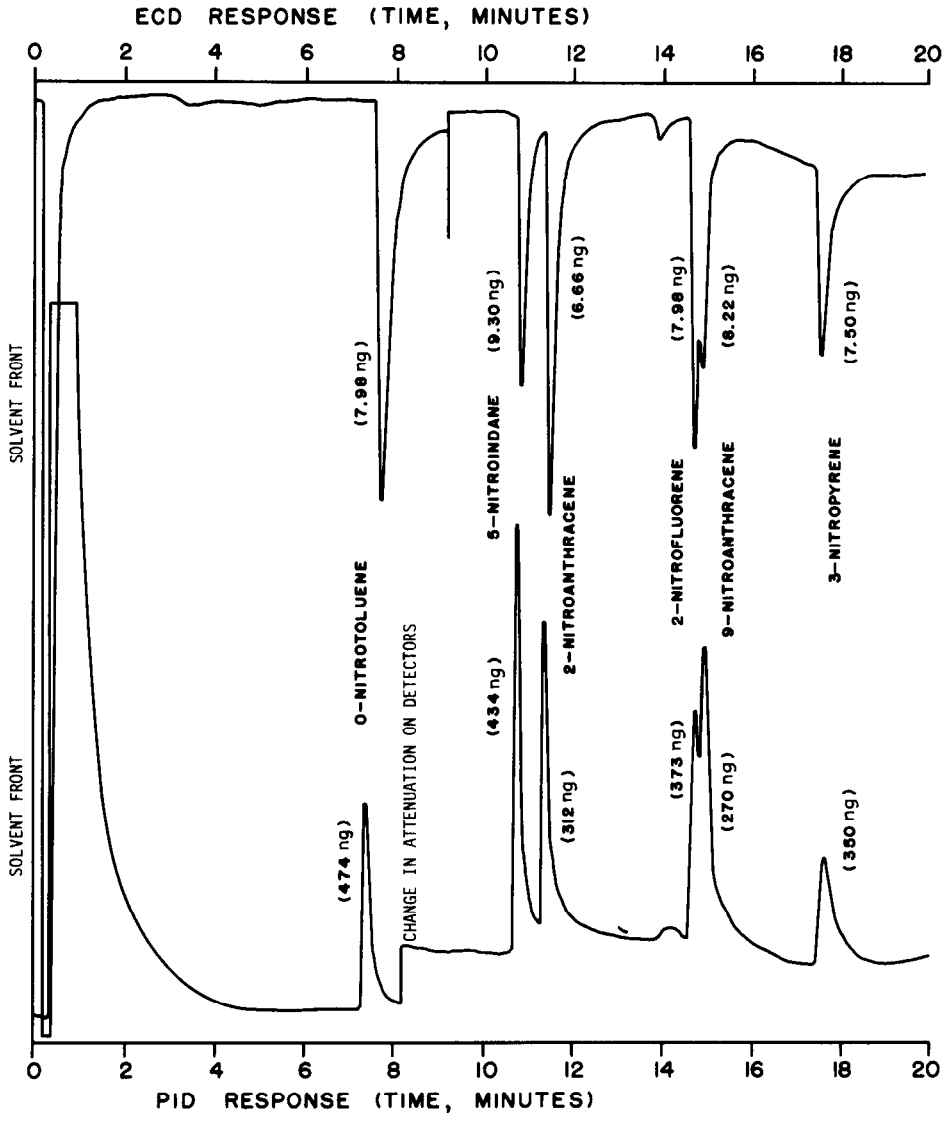


Fig. 5. GC–ECD/PID combined (superimposed) chromatograms for mixture of PAHs and nitro-PAHs with *o*-nitrotoluene internal standard. GC conditions: 6 ft. × 2.0 mm I.D. glass column of Permabond methylsilicone at 40–225°C with programming at 15°C/min; nitrogen carrier gas flow-rate, 40 ml/min, split between ECD and PID.

TABLE V

RELATIVE RESPONSE FACTOR RATIOS ON ECD/PID FOR PAHs AND NITRO-PAHs

ECD/PID relative response factor ratios obtained using GC conditions as in Figs. 4 and 5.

| *Compound pair* | *PID/PID* | *ECD/ECD* | *ECD/PID–ECD/PID** |
|---|---|---|---|
| Indan/5-nitroindan | 0.46 | $3.1 \cdot 10^{-5}$ | $6.80 \cdot 10^{-5}$ |
| Fluorene/2-nitrofluorene | 1.01 | –** | –** |
| Naphthalene/2-nitronaphthalene | 0.23 | $1.70 \cdot 10^{-6}$ | $7.41 \cdot 10^{-6}$ |
| Anthracene/9-nitroanthracene | 0.38 | $2.70 \cdot 10^{-3}$ | $4.88 \cdot 10^{-3}$ |
| Pyrene/3-nitropyrene | 1.00 | $7.0 \cdot 10^{-3}$ | $6.99 \cdot 10^{-3}$ |

* Calculations made using peak heights. Relative response factor normalizations using *o*-nitrotoluene as 1.00 on both detectors.

** Not possible to obtain any measurable ECD response for fluorene at $\mu$g or above levels.

standard. These two chromatograms were obtained separately, using identical GC conditions, but with different levels of the nitro-PAHs injected as a function of the detector in use. The final two chromatograms were purposely superimposed in order to be able to make direct detector comparisons more apparent. Although 2-nitrofluorene and 9-nitroanthracene are not baseline resolved in Fig. 5, separate injections of each of these alone together with the internal standard allowed the direct determination of relative response factors for each detector.

A summary of the PAH and nitro-PAH relative response factors for the ECD and the PID is given in Table IV, normalized and related to *o*-nitrotoluene (base response 1.00 on both detectors). This provides the data in the first two columns, and when the ratios of these normalized RRFs are taken, the final column headed ECD/PID in Table IV is obtained. It is immediately apparent that the PAHs respond orders of magnitude better on the PID than on the ECD, and that the nitro-PAHs have responses on the ECD that are, in general, an order of magnitude or so better (more intense) than on the PID. That is, these two classes of compounds respond in opposite directions, with regard to sensitivity, for these two particular detectors. When the ratios of the RRFs for the ECD/PID (last column in Table IV) are calculated, the overall differences between the PAHs and the nitro-PAH derivatives can be several orders of magnitude. Table V makes this last comparison directly; for each PAH–nitro-PAH pair, their respective PID/PID and ECD/ECD ratios are presented. The final column in Table V, gives the respective ECD/PID–ECD/PID ratios from Table IV for each PAH–nitro-PAH pair, [the ECD/PID ratio from Table IV for a particular PAH was divided by the analogous ECD/PID ratio for its direct nitro-PAH analog (indan/5-nitroindan)]. It is the final column of Table V that is of most interest, because it indicates for the first time that ECD/PID ratios of between 3 and 6 orders of magnitude difference are possible for a given PAH and its corresponding nitro-PAH. This suggests an unusually high degree of selectivity for any particular PAH and its nitro derivative via GC–ECD/PID relative response factors and their derived ratios. As many environmental samples have already been shown to contain PAHs together with nitro-PAHs, this approach should provide a new method of confirming the class of compounds to which an unknown GC peak may belong.

The above analyses and detector response factors for these nitro aromatics,

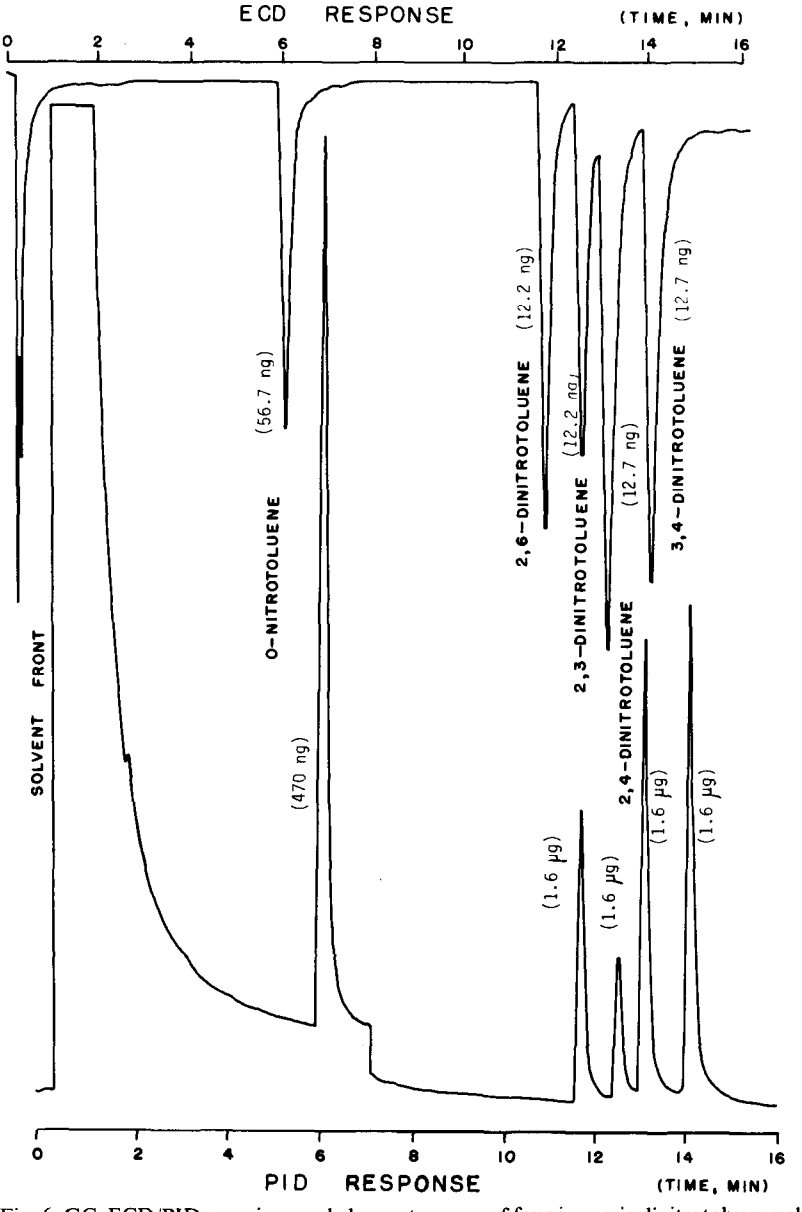


Fig. 6. GC–ECD/PID superimposed chromatograms of four isomeric dinitrotoluenes plus *o*-nitrotoluene. GC conditions: 6 ft. × 2.0 mm I.D. glass column of Permabond PEG 20M at 50–180°C with programming at 10°C/min; nitrogen carrier gas flow-rate, 35–40 ml/min.

PAHs and nitro-PAHs were repeated on Permabond PEG 20M packing material, with GC separation conditions as indicated in Fig. 6. This is a reconstructed GC–ECD/PID set of chromatograms, wherein the GC–ECD and GC–PID chromatograms were obtained separately by two injections of the same mixture of nitro derivatives, but utilizing different levels for each injection. The final two chromatograms

were superimposed to yield Fig. 6 for the sake of simplicity. Whereas it was not previously possible to baseline resolve the 2,3- and 2,4-dinitrotoluene isomers (Fig. 3), with the Permabond PEG 20M packing material this separation is readily achieved. Determinations of RRFs, normalized RRF and ECD/PID ratios of RRFs, as above, were made with the Permabond PEG 20M separations, and these results, as expected, are very similar to those already presented for the Permabond methylsilicone packing material (Table II). Similarly, the PAHs and nitro-PAHs were also studied on this second Permabond packing, and their detector responses, RRFs and similar data agree fairly well with those presented in Tables IV and V.

The data presented above are useful only when the amounts of each nitro aromatic, PAH and nitro-PAH reaching the detectors are within the linear portion of the calibration graph for such compounds on each detector. Clearly, if the amounts being injected are outside the linear portion of the calibration graph, then the ECD/PID ratios so obtained would not be valid or reproducibly useful and/or applicable. Thus, for the analyst to use this entire approach for trace organic analysis, one must first demonstrate that one is indeed working within the linear portion of the calibration graphs for each compound of interest with each detector used. This has now been demonstrated for all of the above data, when individual calibration graphs were obtained for at least one member of each class or group of nitro derivatives with both the ECD and the PID. The amounts of each compound reaching the two detectors in every study have now been shown to fall within the linear portion of the applicable calibration graphs. It is important to remember this whenever ratios of detector responses are to be used as a method of analyte identification and/or confirmation.

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