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Evaluation of a Thermionic Ionization Detector for Nitrated Polycyclic Aromatic Hydrocarbons

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A new, commercially available thermionic ionization detector operated in a nitrogen atmosphere (TID-1-N₂) has been evaluated for detection of nitrated polycyclic aromatic hydrocarbons (nitro-PAH). The detector responded linearly to two nitro-PAH within the approximate concentration ranges of 110 ng to 3 pg per compound. The minimum detectable quantities of 2,2'-dinitrobiphenyl and 9-nitroanthracene were approximately 3 pg per compound ($S/N \approx 3$) using the experimental conditions described in the text. The response per unit concentration of the TID-1-N₂ was not constant for the 45 nitro-PAH investigated. Lastly, the TID-1-N₂ was shown to respond selectively to low levels of nitro-PAH in a complex organic matrix.

In recent years, nitrated polycyclic aromatic hydrocarbons (nitro-PAH) have been recognized as a class of potent chemical mutagens (1-3). Nitropyrenes have been reported to be the most potent mutagens known (4). Nitro-PAH have been found in air particulate matter (5), diesel exhaust particulates (6), carbon black (7), and working atmospheres around an aluminum smelter (8). It is thought that they may be formed as a result of reactions between nitrogen oxides and polycyclic aromatic hydrocarbons (PAH) (2, 9), both of which are present during combustion.

Although nitro-PAH are apparently widespread, they are generally found in trace amounts in the presence of a complex organic matrix. This fact has complicated the gas chromatographic analysis of these compounds, since nitro-PAH must

be separated from potential interferences when a universal gas chromatographic detector is used. When interferences are present, a sensitive and selective gas chromatographic detector must be employed. Selective detection of analytes is often preferable because prefractionation to yield samples that are composed primarily of nitro-PAH represents an additional step in the analytical procedure that could ultimately lead to decreased quantitative precision.

Numerous analytical techniques have been applied to the analysis of nitro-PAH, including gas chromatography using both universal and selective detectors. The importance of selective detectors is emphasized by the fact that nitro-PAH are usually present in trace amounts, and unless a sensitive and selective detector is employed, these compounds are obscured by large amounts of coeluting interferences. Ramdahl et al. (10) have evaluated the simultaneous use of flame-ionization and thermionic nitrogen/phosphorus detection (NPD) to facilitate the identification of nitro-PAH; the use of both detectors simplified complex chromatographic profiles and permitted nitro-PAH to be distinguished from other sample components. Oehme et al. (8) have evaluated the use of an alkali salt flame-ionization detector (nitrogen sensitive) and a conventional flame-ionization detector by analyzing a sample for nitro-PAH that was rich in carbazoles. These workers found that "in comparison to the flame-ionization detector (FID), the NPD did not give any improvement in selectivity." Oehme et al. (8) also evaluated the simultaneous use of an electron capture detector (ECD) and a FID. They found that nitro-PAH are detected with excellent sensitivity and selectivity; the detection limit for 2-nitrofluorene was 1-2 pg (S/N

= 10). Unfortunately, the ECD did not respond uniformly to all nitro-PAH. Response factors of nitro-PAH varied by a factor of 60 relative to 2-nitrofluorene.

Possibly the most selective and sensitive gas chromatographic detector used to date for analysis of nitro-PAH is mass spectrometry employing negative ion chemical ionization (NICIMS). Oehme et al. (8) and Ramdahl and Urdal (11), as well as Newton et al. (12), have successfully employed NICIMS for analysis of nitro-PAH in complex mixtures. Using NICIMS, Oehme et al. (8) reported a detection limit for 2-nitrofluorene of approximately 100 pg ($S/N = 10$) in the scanning mode and between 2 and 4 pg when the spectrometer was operated in the single ion monitoring mode. Major disadvantages of NICIMS for routine analysis of nitro-PAH are the expense of the instrumentation and the lack of reference spectra.

Patterson et al. (13-15) have recently introduced two thermionic ionization detectors for gas chromatography. One of these detectors contains a high concentration of Cs in its source, which consequently lowers the work function potential of the surface. Preliminary data from the use of this detector indicated that when it is operated in a nitrogen atmosphere (TID-1-N₂), it showed a very high degree of sensitivity and specificity for compounds containing electronegative functionality, particularly nitrated compounds. When operated in a nitrogen atmosphere, the detector's source surface temperature is between 300 °C and 600 °C, and the gaseous boundary layer is not chemically reactive. Thus, electronegative functional groups must be present in the sample itself in order for it to decompose into electronegative products. The ionization process is thought to be the removal of electrons from the thermionic source to form negative ions in the gas phase. According to Patterson et al. (13-15), not all molecules containing an electronegative substituent give a response from the TID-1-N₂. For example, 2,6-dinitrotoluene and 2,4-dinitrotoluene respond, while nitrobenzene does not (15).

In the present investigation, a thermionic ionization detector operated in a nitrogen atmosphere has been evaluated for analysis of nitro-PAH. The linear dynamic range, the minimum detectable quantities, and the selectivity of the detector toward nitro-PAH have been investigated by using well-defined operating conditions.

EXPERIMENTAL SECTION

A Varian 3700 gas chromatograph equipped for capillary use was fitted with a Detector Engineering and Technology thermionic ionization detector, a Varian thermionic specific detector power supply, and a Varian CDS-101 chromatographic data system. The detector was operated by using N₂ as a detector gas at a flow rate of 93 mL/min, a temperature of 300 °C, a bias voltage of -12 V, and bead currents ranging from 3.2 to 3.6 A. The column was 30 m × 0.20 mm fused-silica coated with a 0.25- μ m film of SE-52, employing helium as a carrier gas at an average linear velocity of 46 cm/s at 25 °C. Graphite ferrules were used to make column connections. Methylene chloride solutions of samples were introduced by using splitless injection (a 45-s splitless period) into a 300 °C injector. The nitro-PAH studied were used as received from the supplier.

The linear dynamic range of the TID-1-N₂ detector toward 2,2'-dinitrobiphenyl and 9-nitroanthracene was evaluated over a wide concentration range by using two different detector bead currents. A methylene chloride (distilled in glass, Burdick and Jackson) solution containing approximately 85 ng/ μ L of 2,2'-dinitrobiphenyl and 110 ng/ μ L of 9-nitroanthracene was prepared and analyzed by using the aforementioned column and conditions as well as linear temperature programming from 25 °C to 217 °C at 4 °C/min. The TID-1-N₂ was operated at a bead current of 3.2 A. The maximum current the detector can be operated at is 4.0 A. The solution was diluted and each dilution analyzed under the same conditions. When the concentration of analytes was approximately 2 ng each, the detector response was just observable using a bead current of 3.2 A. The bead current was

then changed to 3.4 A. The sample was diluted and analyzed. This process was continued until signals resulting from these compounds were no longer observable at a bead current of 3.4 A.

To evaluate the relative response of the TID-1-N₂ to nitro-PAH, methylene chloride solutions containing a wide variety of nitro-PAH were analyzed. The Varian 3700 gas chromatograph was temperature-programmed from 25 °C to 300 °C at 4 °C/min. These same solutions were also analyzed with a HP-5840 gas chromatograph equipped for capillary use and fitted with a FID. Separations using the HP-5840 gas chromatograph were achieved by using a 30-m × 0.20-mm fused-silica column coated with a 0.25- μ m film of SE-52, and helium carrier gas having an average linear velocity of 50 cm/s at 25 °C. Samples were injected in the splitless mode (a 45-s splitless period) and linear temperature programmed from 25 °C to 300 °C at 4 °C/min.

The selectivity of the TID-1-N₂ was evaluated by preparing a solution of known amounts of 11 nitro-PAH in a complex organic matrix. The aromatic fraction of a Homestead, KY, coal extract, 4.4 mg, was diluted to 10.0 mL with methylene chloride in a volumetric flask. The resulting solution was analyzed with the aforementioned HP-5840 gas chromatograph and linear temperature programming from 25 °C to 297 °C at 4 °C/min. The sample was also analyzed by use of the previously described Varian 3700 equipped with a TID-1-N₂ and temperature programmed from 25 °C to 265 °C at 4 °C/min. This chromatographic profile is an experimental blank, and no peaks were observed when employing the TID-1-N₂. A methylene chloride solution of nitro-PAH was then added in 0.1-mL increments to a 1.0-mL aliquot of the methylene chloride solution of the coal extract aromatic fraction. After each 0.1-mL addition of nitro-PAH solution, the spiked sample was analyzed with a FID on the HP-5840 as well as a TID-1-N₂ on the Varian 3700.

RESULTS AND DISCUSSION

The linear dynamic range of the TID-1-N₂ with respect to 2,2'-dinitrobiphenyl and 9-nitroanthracene was evaluated within wide concentration ranges by preparing a solution containing approximately 85 ng/ μ L of 2,2'-dinitrobiphenyl and 110 ng/ μ L of 9-nitroanthracene. The response of the detector was linear with respect to both compounds at two different detector bead currents. The chromatographic peak heights of these compounds as a function of the amount of analyte injected was studied by using bead currents of 3.2 A and 3.4 A. The TID-1-N₂ sensitivity is a function of bead current. In general, the higher the bead current, the more sensitive the detector and the higher the background signal. Chromatographic peak heights obtained at 3.2 A of approximately 85, 31, 3.6, and 1.8 ng of 2,2'-dinitrobiphenyl were graphed. The linear least-squares regression line had a slope of 14.76 and a y intercept of 12.51 with a correlation coefficient of 0.99. The same procedure was used on data obtained from approximately 110, 40, 4.6, and 2.3 ng of 9-nitroanthracene. The linear least-squares regression line had a slope of 12.34, a y intercept of 34.16, and a correlation coefficient of 0.99. At 3.2-A bead current, the response of the detector toward approximately 2 ng of these two compounds is just discernible. The bead current was then increased to 3.4 A, and the linear dynamic range with respect to these compounds was studied down to 2.5 pg and 3 pg, respectively. The linear least-squares regression lines of graphs of approximately 383, 25, 12, 6, and 3 pg of 9-nitroanthracene and 300, 20, 10, 5, and 2.5 pg of 2,2'-dinitrobiphenyl as a function of chromatographic peak height had a slope of 3675, a y intercept of 8.64, and correlation coefficient 0.99 for 9-nitroanthracene and a slope of 1937, a y intercept of 4.62, and a correlation coefficient of 0.99 for 2,2'-dinitrobiphenyl, respectively. The TID-1-N₂ displayed linear response within the concentration ranges studied. Over the concentration range of approximately 110 ng/ μ L to 2 ng/ μ L, when equal weights of 2,2'-dinitrobiphenyl and 9-nitroanthracene were analyzed using a bead current of 3.2 A, the chromatographic peak resulting from 2,2'-dinitrobiphenyl

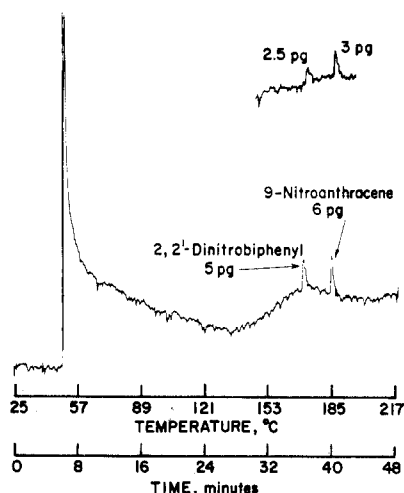


Figure 1. Chromatographic profiles of 5 and 2.5 pg of 2,2'-dinitrobiphenyl and 6 and 3 pg of 9-nitroanthracene, obtained using a TID-1-N₂ bead current of 3.4 A.

was larger; however, this situation changes when the response of these compounds is investigated over the concentration range of approximately 0.38 ng/ μ L to 2.5 pg/ μ L, using a bead current of 3.4 A. The reasons for this change are not clear although it appears to be caused by the increase in detector bead current. Nevertheless, the important point to recognize is that the response of the TID-1-N₂ is linear at any one bead current and therefore could be used for quantitative analysis of nitro-PAH. Detector response toward these two compounds was linear at 3.2 A and at 3.4 A, but the slopes of the linear least-square regression lines describing detector response with respect to these compounds changed when bead current changed.

The minimum detectable quantities of 2,2'-dinitrobiphenyl and 9-nitroanthracene were determined. It should be recognized that the minimum detectable quantity is strongly dependent upon experimental conditions of bead current, detector temperature, temperature-program rate, and other instrumental parameters. The minimum detectable quantities of 2,2'-dinitrobiphenyl and 9-nitroanthracene at a signal to noise ratio of about 3 were approximately 3 pg ($S/N \approx 3$) of each compound. A chromatographic profile of approximately 2.5 pg of 2,2'-dinitrobiphenyl and 3 pg of 9-nitroanthracene appears in Figure 1 and was obtained by using a detector bead current of 3.4 A, a detector temperature of 300 °C, and linear temperature programming from 25 °C to 217 °C at 4 °C/min.

During the course of evaluating the TID-1-N₂, it became clear that detector response was not uniform toward all nitro-PAH. Although the response factors of a variety of individual compounds was not rigorously investigated, the limited investigation described here indicated that response factors differed from analyte to analyte by as much as 100-fold. Patterson et al. (14, 15) have previously observed that the TID-1-N₂ responded to 2,4-dinitrotoluene and 2,6-dinitrotoluene but not to nitrobenzene. This observation led Patterson to conclude that detector response was a function of molecular structure and "how these electronegative functionalities are bound up in the molecular structure of the analyte" (15). Our experience has been that the TID-1-N₂ responds to all nitro-PAH investigated but that the response from equal amounts of different nitro-PAH is very different. To obtain some measure of these response differences, a methylene chloride solution of 45 nitro-PAH and 4 PAH was analyzed with a FID and a TID-1-N₂. The chromatographic profiles obtained are in Figures 2 (FID) and 3 (TID-1-N₂). The numbered chromatographic peaks in both profiles are listed in Table I, along with the approximate amount of each nitro-PAH. Although it appears from comparing the chroma-

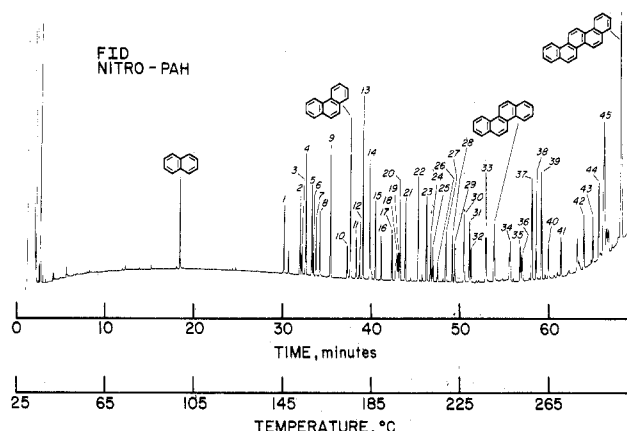


Figure 2. Chromatographic profile of a methylene chloride solution containing 45 nitro-PAH obtained using a FID. Numbered chromatographic peaks are identified in Table I. This same sample was analyzed with a TID-1-N₂; see Figure 3.

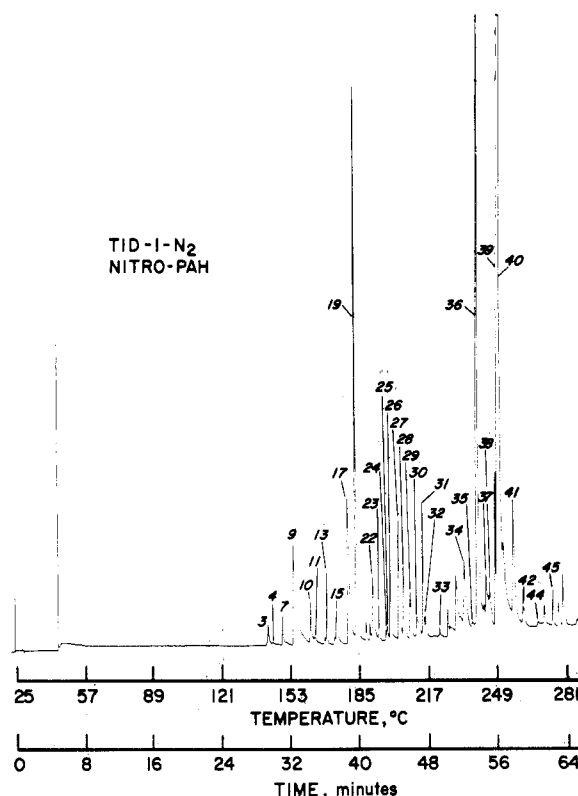


Figure 3. Chromatographic profile of a methylene chloride solution containing 45 nitro-PAH obtained using a TID-1-N₂. Numbered chromatographic peaks are identified in Table I. This same sample was analyzed with a FID; see Figure 2.

tographic profiles in Figures 2 and 3 that the TID-1-N₂ does not respond to a variety of nitro-PAH (such as 5-nitroindan), this seeming lack of response is because the electrometer attenuation was adjusted to keep most peaks on scale. This fact is illustrated in Figure 4, which is a chromatographic profile of a second solution containing a different distribution of nitro-PAH analyzed by using the TID-1-N₂. Numbered chromatographic peaks are identified in Table I. In this case, the TID-1-N₂ responds to 5-nitroindan and other nitro-PAH. Comparison of Figures 2 and 3, along with the concentration information in Table I, allows a visual estimation of the relative response of the TID-1-N₂ to a variety of nitro-PAH. Response factors of nitro-PAH relative to a standard were not investigated because peak heights and thus relative peak heights among compounds can be a function of injection technique as well as the absorptive nature of the chromato-

Table I. Amounts of Nitro-PAH Present in the Sample Analyzed in Figures 2 and 3

nitro-PAH		ng in- source ^a injected		nitro-PAH		ng in- source ^a injected	
1	5-nitroindan	Aldrich	26	24	3-nitro-9-fluorenone	Aldrich	23
2	5-nitro-1,2,3,4-tetrahydronaphthalene	ABC	32	25	9-nitroanthracene	Aldrich	21
3	5-nitroquinoline	Aldrich	13	26	1,8-dinitronaphthalene	Aldrich	10
4	1-nitronaphthalene	Aldrich	47	27	2-nitro-9-fluorenone	ABC	28
5	5-nitro-6-methylquinoline	ICN	36	28	2,4-dinitro-2'-methylbiphenyl ether	ABC	27
6	1-nitro-2-methylnaphthalene	ICN	12	29	2,2'-dinitrobiphenyl	Aldrich	21
7	2-nitronaphthalene	Aldrich	20	30	2-nitroanthracene	SBT	48
8	6-nitroquinoline	Aldrich	30	31	9-methyl-10-nitroanthracene	SBT	37
9	2-nitrobiphenyl	Aldrich	47	32	1-methyl-9-nitrophenanthrene	SBT	26
10	8-nitroquinoline	Aldrich	14	33	7-nitro-3,4-benzocoumarin	Aldrich	65
11	8-nitroquinaldine	ABC	18	34	3-nitrofluoranthene	SBT	26
12	8-nitro-7-methylquinoline	ICN	11	35	1-nitropyrene	ABC	28
13	3-nitrobiphenyl	Aldrich	75	36	2,6-dinitro-9-fluorenone	ABC	16
14	4-nitrobiphenyl	Aldrich	50	37	2,5-dinitrofluorene	RDH	29
15	4-nitrophenyl phenyl ether	ABC	18	38	2,7-dinitro-9-fluorenone	Aldrich	27
16	1,4-dinitronaphthalene	ABC	18	39	4-nitro- <i>p</i> -terphenyl	Aldrich	71
17	1,5-dinitronaphthalene	RDH	26	40	1,3,6,8-tetranitronaphthalene	ABC	12
18	4-nitroquinoline <i>n</i> -oxide	Aldrich	10	41	2,2'-dimethyl-4,4'-dinitrobiphenyl	Aldrich	26
19	1,3-dinitronaphthalene	Aldrich	62	42	1,3-dinitropyrene	DS	24
20	3-nitrodibenzofuran	CS	39	43	1,6-dinitropyrene	DS	19
21	5-nitroacenaphthene	IIT	33	44	1,8-dinitropyrene	DS	28
22	2,2'-dinitrobiphenyl	RDH	50	45	2,4,5,7-tetranitro-9-fluorenone	Aldrich	27
23	2-nitrofluorene	Aldrich	45				

^a Aldrich, Aldrich Chemical Co.; ICN, ICN Pharmaceuticals, Inc.; ABC, Alfred Bader Library of Specialty Chemicals; RDH, Riedel-de Haen; CS, Chem Service, Inc.; IIT, Illinois Institute of Technology Research Institute; SBT, Silvester B. Tejada, U.S. E.P.A.; DS, Dennis Schuetzle, Ford Motor Co.

graphic system. Thus, even when using universal detectors and capillary columns, relative response factors determined under one set of operating conditions at one laboratory are not usually transferable to other operating conditions or other laboratories. Additionally, the effects of detector operating conditions appear to have a large impact on relative peak heights when using the TID-1-N₂, further decreasing the overall usefulness of relative response factors. For example, relative peak heights of 2,2'-dinitrobiphenyl and 9-nitroanthracene changed when bead current was increased from 3.2 A to 3.4 A.

Note that many of the chromatographic peaks tail on the chromatographic profiles obtained using the TID-1-N₂. When the same samples were analyzed with the same gas chromatograph and column under identical conditions except employing a FID, these peaks did not tail. Peak tailing may be caused by adsorption of the analyte or its thermal decomposition products on the detector surface or by excessive detector void volume.

The selectivity of the TID-1-N₂ was evaluated by adding a methylene chloride solution of nitro-PAH to a methylene chloride solution of the aromatic fraction of a Homestead, KY, coal extract. This aromatic fraction is extremely complex, and therefore its presence ensured that the added nitro-PAH would coelute with PAH (16). The nitro-PAH were added to the methylene chloride solution of coal extract in 0.10-mL increments. After each addition of nitro-PAH, the spiked sample was analyzed by gas chromatography employing a FID and a TID-1-N₂. After the first 0.1-mL addition of nitro-PAH, chromatographic peaks resulting from the detection of nitro-PAH were observed with the TID-1-N₂. However, it was not until 0.5 mL of the nitro-PAH solution had been added that the chromatographic peaks caused by the added nitro-PAH were readily distinguishable in the chromatographic profile obtained by using the FID. The chromatographic profiles obtained by using a FID and a TID-1-N₂ are shown in Figure 5. Numbered chromatographic peaks are listed in Table II, along with the approximate concentration of individual nitro-PAH in the spiked solution. The TID-1-N₂ did not respond to PAH, while the nitro-PAH were readily ob-

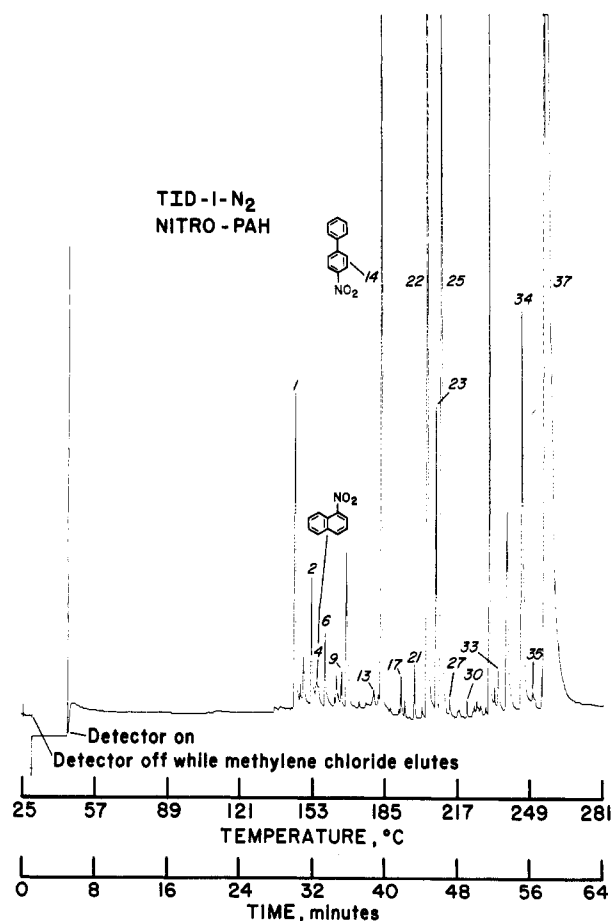


Figure 4. Chromatographic profile of a second methylene chloride solution of nitro-PAH obtained with a TID-1-N₂. This solution contained a different distribution of nitro-PAH than that chromatographed in Figure 3. Numbered chromatographic peaks are identified in Table I.

served. Analysis of the unspiked methylene chloride solution of the coal extract aromatic fraction using the TID-1-N₂ showed no chromatographic peaks. This clearly demonstrates

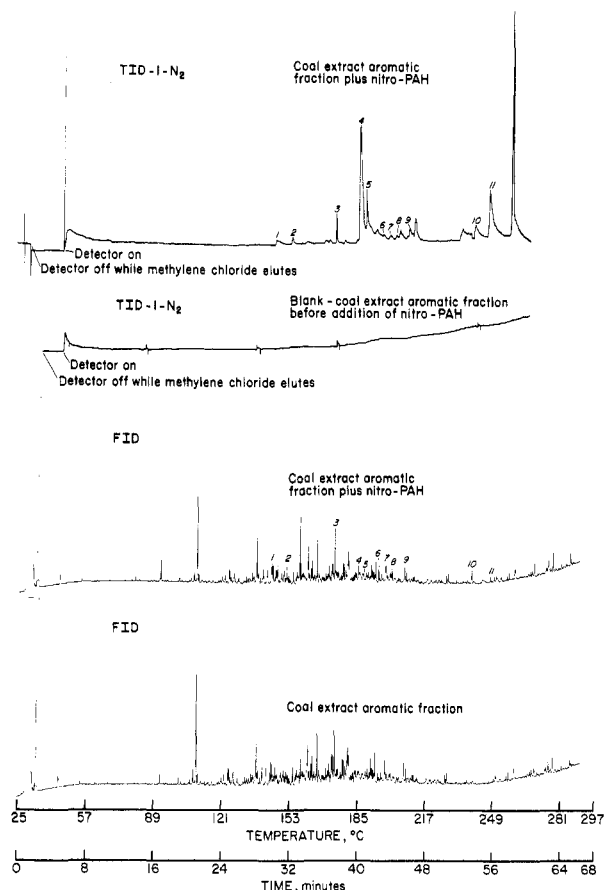


Figure 5. Chromatographic profiles of a coal extract aromatic fraction before and after addition of nitro-PAH, using either a FID or a TID-1-N₂. Numbered chromatographic peaks are identified in Table II, along with the approximate amounts of each nitro-PAH added. The bottom chromatographic profile, of a methylene chloride solution of the aromatic fraction of a coal extract, was obtained with a FID on a HP-5840 gas chromatograph. The middle chromatographic profile was obtained by using the same conditions as the bottom profile after addition of 0.5 mL of a methylene chloride solution of nitro-PAH to 1.0 mL. The top chromatographic profile of coal extract was obtained after addition of 0.5 mL of a methylene chloride solution of nitro-PAH to 1.0 mL of a methylene chloride solution of the aromatic fraction of a coal extract. The top profile was obtained with a TID-1-N₂ on a Varian 3700.

Table II. Concentration of Nitro-PAH Spiked into the Coal Extract Aromatic Fraction (See Figure 5)

	compound	ng/ μ L
1	5-nitro-1,2,3,4-tetrahydronaphthalene	42
2	1-nitro-2-methylnaphthalene	13
3	3-nitrobiphenyl	27
4	1,5-dinitronaphthalene	33
5	3-nitrodibenzofuran	29
6	2,2'-dinitrobiphenyl	52
7	2-nitrofluorene	25
8	9-nitroanthracene	53
9	2-nitro-9-fluorenone	14
10	1-nitropyrene	54
11	2,5-dinitrofluorene	35

the selectivity of the TID-1-N₂ toward nitro-PAH.

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Registry No. 5-Nitroindan, 7436-07-9; 5-nitro-1,2,3,4-tetrahydronaphthalene, 29809-14-1; 5-nitroquinoline, 607-34-1; 1-nitronaphthalene, 86-57-7; 5-nitro-6-methylquinoline, 23141-61-9; 1-nitro-2-methylnaphthalene, 881-03-8; 2-nitronaphthalene, 581-89-5; 6-nitroquinoline, 613-50-3; 2-nitrobiphenyl, 86-00-0; 8-nitroquinoline, 607-35-2; 8-nitroquinoline, 881-07-2; 8-nitro-7-methylquinoline, 7471-63-8; 3-nitrobiphenyl, 2113-58-8; 4-nitrobiphenyl, 92-93-3; 4-nitrophenyl phenyl ether, 620-88-2; 1,4-dinitronaphthalene, 6921-26-2; 1,5-dinitronaphthalene, 605-71-0; 4-nitroquinoline *n*-oxide, 56-57-5; 1,3-dinitronaphthalene, 606-37-1; 3-nitrodibenzofuran, 5410-97-9; 5-nitroacenaphthene, 602-87-9; 2,2'-dinitrobiphenyl, 2436-96-6; 2-nitrofluorene, 607-57-8; 3-nitro-9-fluorenone, 42135-22-8; 9-nitroanthracene, 602-60-8; 1,8-dinitronaphthalene, 602-38-0; 2-nitro-9-fluorenone, 3096-52-4; 2,4-dinitro-2'-methyldiphenyl ether, 2363-26-0; 2,2'-dinitrobiphenyl, 16968-19-7; 2-nitroanthracene, 3586-69-4; 9-methyl-10-nitroanthracene, 84457-22-7; 1-methyl-9-nitrophenanthrene, 87517-97-3; 7-nitro-3,4-benzocoumarin, 22371-68-2; 3-nitrofluoranthene, 892-21-7; 1-nitropyrene, 5522-43-0; 2,6-dinitro-9-fluorenone, 58160-30-8; 2,5-dinitrofluorene, 15110-74-4; 2,7-dinitro-9-fluorenone, 31551-45-8; 4-nitro-*p*-terphenyl, 10355-53-0; 1,3,6,8-tetranitronaphthalene, 28995-89-3; 2,2'-dimethyl-4,4'-dinitrobiphenyl, 87517-98-4; 1,3-dinitropyrene, 75321-20-9; 1,6-dinitropyrene, 42397-64-8; 1,8-dinitropyrene, 42397-65-9; 2,4,5,7-tetra-nitro-9-fluorenone, 746-53-2.

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