LIBRARY OF CHROMATOGRAMS ILLUSTRATING THE UNIQUE CHEMICAL SELECTIVITY PROVIDED BY TID-1 SURFACE IONIZATION DETECTION

(March 2008)

Introduction to the TID-1 Surface Ionization Process. TID-1 Surface Ionization Detection is an easy modification of the basic equipment used for Nitrogen-Phosphorus Detection (NPD) on Agilent 6890/7890, Thermo Fisher Scientific, and SRI Instruments GC models, and for DET NPD equipment that retrofits on Varian and HP 5890 GC models.

In the Agilent and DET equipment, the detector configuration consists of a cylindrically shaped, ceramic coated ion source located on the axis of a concentric collector cylinder as depicted in Figure 1. The conversion from an NPD involves changing to a TID-1 type ion source, and changing to an inert detector gas environment of Nitrogen, or an oxidizing gas environment of Air or Oxygen (i.e., no Hydrogen is required).

One of the important operating parameters in thermionic ionization detectors is the ion source temperature. That is controlled by a power supply that provides heating current through the wire core of the ion source. In TID-1 detection, the ion source typically operates at a surface temperature of 400 - 600°C versus the 600 - 800°C that is required for NP detection.

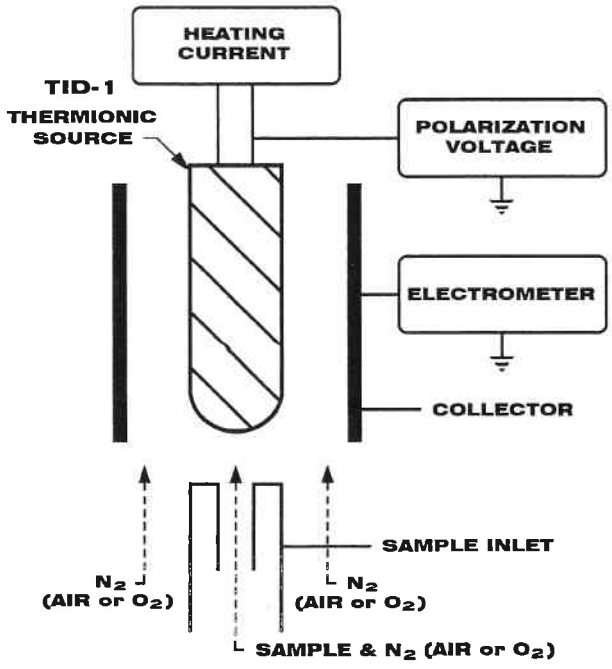


Figure 1. Schematic illustration of a TID-1 detector.

The detector power supply also polarizes the ion source at a negative voltage relative to the surrounding collector. For NP detection, a low polarization of - 5 V or less generally provides the best signal to noise and the best selectivity versus hydrocarbons. The unique selectivity provided by TID-1 detection can also be achieved at the low NPD polarization. However, TID-1 sensitivity and detectivity is greatly improved by using higher polarizations. For example, with a DET Current Supply used to power the ion sources, a polarization of -5 V works best for an NPD, and a polarization of - 45 V works best for TID-1 detection.

Unlike an NPD, TID-1 detection does not involve any gas phase sample decomposition in an ignited Hydrogen-Air gas environment. Instead, negative ion species formed in TID-1 detection are the result of direct impact of sample compounds with the hot ion source surface. Ions formed at the surface then migrate through the surrounding gas to the collector where they are measured for the detector signal. The magnitude and selectivity of the detector signal depends on the temperature of the ionizing surface, as well as whether that surface is in an inert or oxidizing gas environment. In addition, the magnitude of the detector signal depends strongly on the detailed molecular structure of the sample compound. TID-1 response to different compound structures can be classified according to the following categories:

primary response - compound detectivities of 1 pg or less;
secondary response - compound detectivities in the range of 1 - 100 pg;
tertiary response - compound detectivites in the range of 0.1 - 100 ng;
macro response - compound detectivities greater than 0.1 µg.

This report illustrates TID-1 detector responses to compounds in each of these categories. Most of the chromatograms shown here demonstrate a selective detection capability unlike any other GC detector.

Exceptional Sensitivity and Selectivity Compounds Containing the NO_2 Functional Group.

The TID-1 ionization process forms negatively charged ion species, and compounds containing the strongly electronegative NO_2 functional group are among the compound types that are the best primary responders. The specific location of the NO_2 group (or groups) within a compound's molecular structure is also a very important factor in determining the magnitude of TID-1 response. This is well illustrated by the comparison of NPD and TID-1 responses in Figure 2, and by the corresponding comparison of molecular structures in Figures 3 and 4. TID-1 signals for 2,4-Dinitrotoluene (peak 8), TNT (peak 11), and 2-Amino-4,6-dinitrotoluene (peak 16) were exceptionally large compared to the other Nitro compounds in the sample. Each of these 3 compounds has an NO_2 group located in a para location relative to other functionalities in the molecular structures. Figure 2 also illustrates another feature of a TID-1 detector which is that it is non-destructive. Consequently, it can be combined in series with another detector like the NPD.

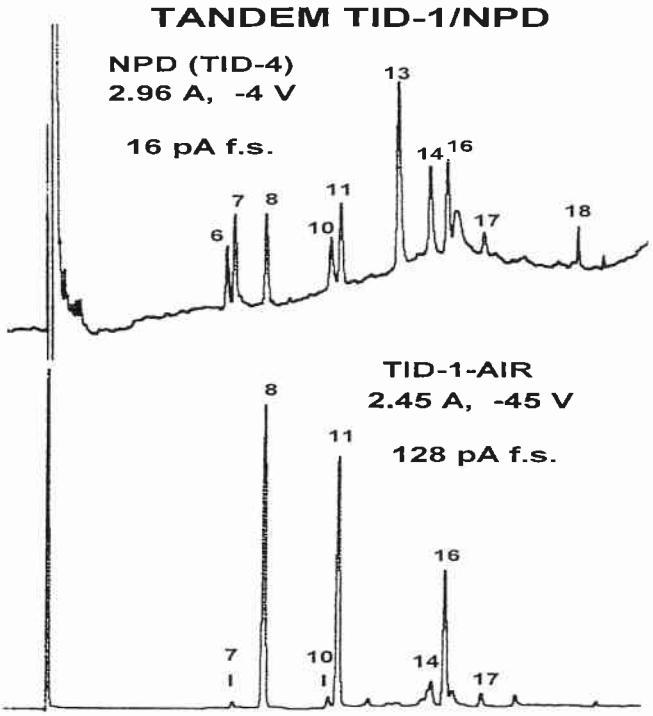


Figure 2. Comparison of NPD and TID-1 responses using a Tandem combination of both detectors mounted on a Varian 3800 GC - both signals generated simultaneously from the same **Nitro Explosives** sample injection. Sample consisted of 200 pg each of: 6=1,3-dinitrobenzene; 7=2,6-dinitrotoluene; 8=2,4-dinitrotoluene; 10=1,3,5-trinitrobenzene; 11=TNT; 13=RDX; 14=4-amino-2,6-dinitrotoluene; 16=2-amino-4,6-dinitrotoluene; 17=tetryl; 18=HMX.

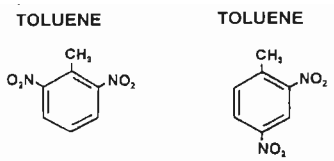


Figure 3. Comparison of molecular structures for peaks 7 and 8 in Figure 2.

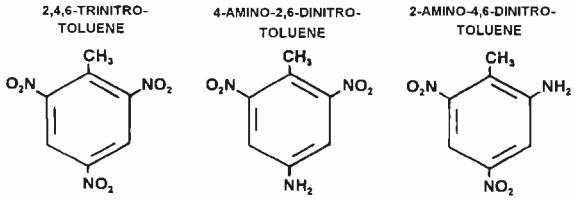


Figure 4. Comparison of molecular structures for peaks 11, 14, and 16 in Figure 2..

As will be discussed later, TID-1 detection provides a tertiary level of selective response to aldehydes. However, when the aldehydes are subjected to derivatization with 2,4-Dinitrophenylhydrazine (2,4-DNPH) according to a widely used analytical method, their detectivity is increased a thousand-fold to a primary level of TID-1 response. This is illustrated in Figure 5.

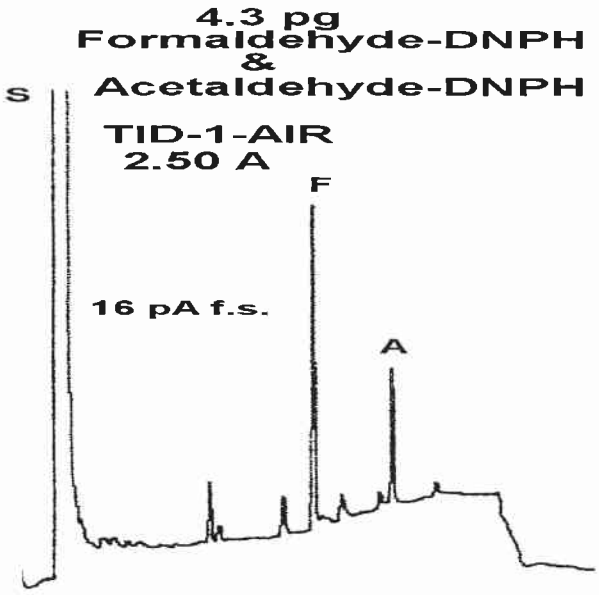


Figure 5. 4.3 pg each of Formaldehyde-DNPH (F) and Acetaldehyde-DNPH (A). S=Methanol solvent and 440ng Acetonitrile. Femtogram detectivities for both aldehydes.

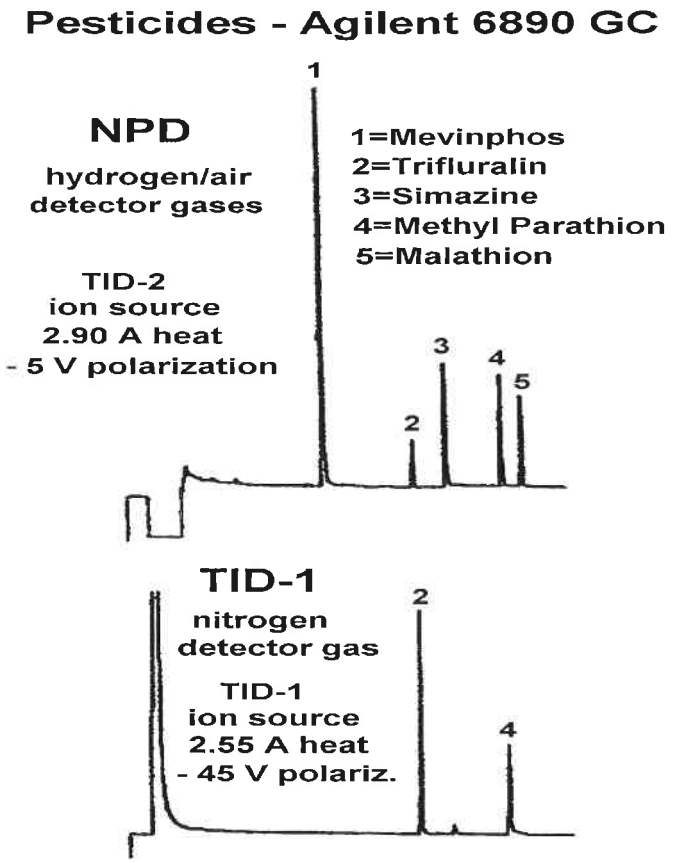


Figure 6. Analysis of N and P pesticides using Agilent 6890 NPD hardware and electrometer with ion sources powered by a DET Current Supply.

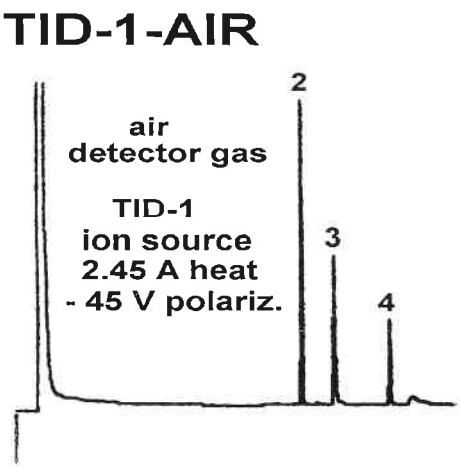


Figure 7. Same sample as Figure 6, but with Air as the TID-1 detector gas instead of Nitrogen.

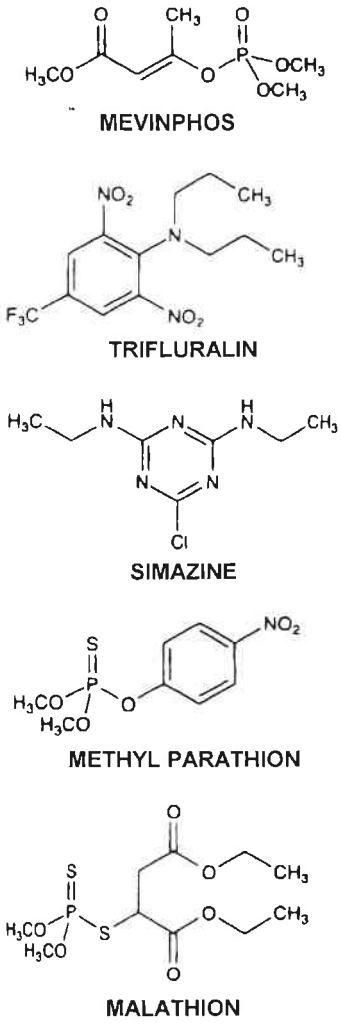


Figure 8. Molecular structures of the components in the sample analyzed in Figures 6 and 7.

Figures 6 and 7 show a comparison of NPD and TID-1 chromatograms for a sample containing a mixture of N and P pesticides whose molecular structures are shown in Figure 8. With an inert detector gas environment of Nitrogen, the TID-1 detector selectively responded to the 2 sample components containing the NO_2 functional group (i.e., Trifluralin and Methyl Parathion). However, when the detector gas was changed to an oxidizing environment of Air, then the TID-1 detector also provided a response to the Simazine component of the sample. The Simazine response can be attributed to the electronegative Cl atom in that molecule.

Exceptional Sensitivity and Selectivity for Compounds Containing Cl Atoms.

Figure 9 shows a TID-1 chromatogram of a mixture of Nitro and Chloro Phenols. The 4-Nitrophenol component (peak 5) produced the largest signal, but Pentachlorophenol (peak 6) and 2,4,6-Trichlorophenol (peak 4) also responded at a primary level of TID-1 response. The other 3 components of the sample were secondary TID-1 responders. Comparison of the large 4-Nitrophenol signal versus the smaller 2-Nitrophenol (peak 2) again demonstrates the strong preference of TID-1 ionization for an NO_2 functional group located in a para position versus other molecular configurations.

Figure 10 compares TID-1 response to Pentachlorophenol versus response to Hexachlorobenzene. The amount of Pentachlorophenol in this sample was 10 times less than that of Hexachlorbenzene, yet its TID-1 sensitivity (i.e., signal per sample weight) was 150 times greater. Clearly, the TID-1 surface has a strong ionizing preference for the OH group rather than another Cl in the sixth position on the chlorinated benzene ring.

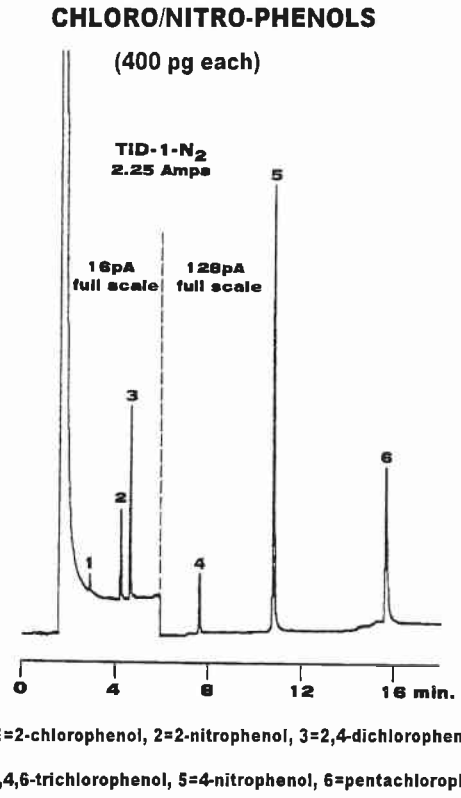


Figure 9. TID-1 detection on Agilent 6890. 400 pg each of 1=2-chlorophenol, 2=2-nitrophenol, 3=2,4-dichlorophenol, 4=2,4,6-trichlorophenol, 5=4-nitrophenol, 6=pentachlorophenol.

Figure 11 shows the analysis of a chlorinated pesticide mixture, and comparison of TID-1 detection versus a TID-3 mode of thermionic detection. The TID-3 data showed responses to all 6 components of the sample, while the TID-1 data exhibited very large primary responses to just a few of the sample components. With a Nitrogen gas environment, large TID-1 responses were generated for Heptachlor (peak 2), Dieldrin (peak 4), and to a lesser extent Endrin (peak 5). When the Nitrogen was replaced by a detector gas environment of Oxygen, the Heptachlor and Dieldrin responses were greatly diminished, and the relative response to Endrin was greatly enhanced. Endrin and Dieldrin are stereoisomers, and it is especially interesting to see that the presence or absence of Oxygen in the detector gas environment can dramatically alter the relative ionization of one isomer versus the other.

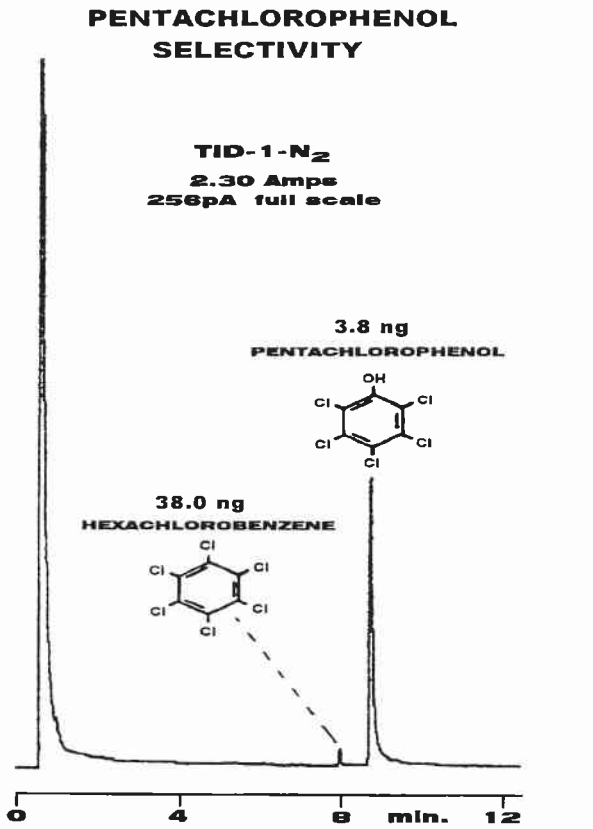


Figure 10. Sample had 10 times more hexachlorobenzene than pentachlorophenol, but pentachlorophenol had the much larger signal.

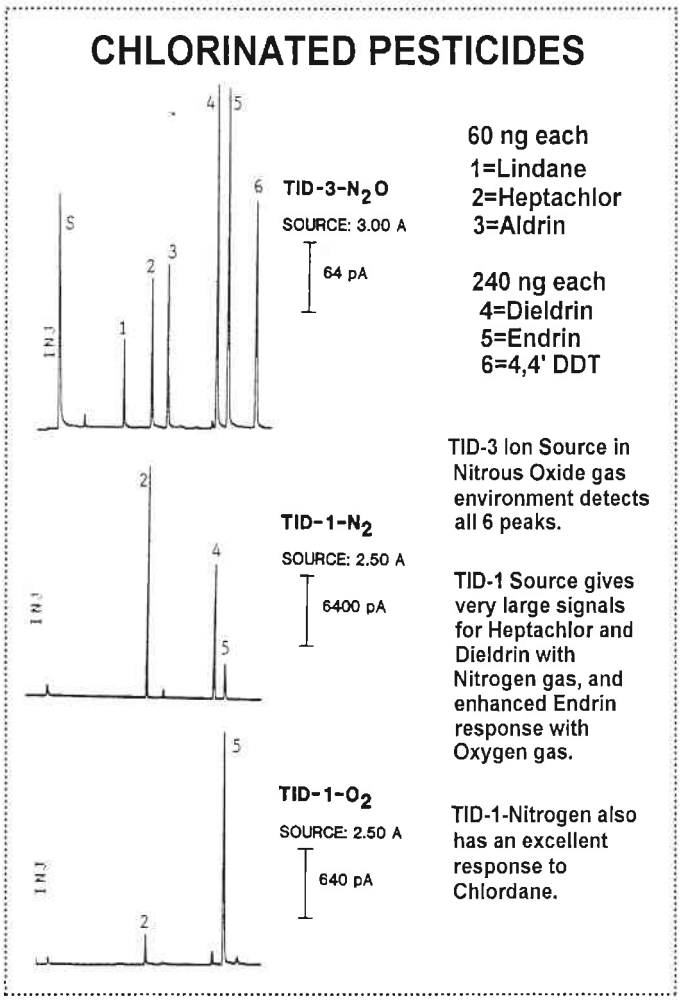


Figure 11. DET TID-1 & TID-3 detectors on a Varian 3800 GC.

Figure 12 demonstrates the unique TID-1 selectivity for Chlordane versus Toxaphene. Both pesticides are characterized by chromatograms containing many peaks. TID-1 responds to Chlordane but not Toxaphene, so the Chlordane peak pattern was readily identified despite a mixture containing 10 times larger concentration of Toxaphene. Figure 13 compares the molecular structures of Heptachlor, Endrin, and Chlordane. A common feature is the presence of a sub-structure containing a similar array of 6 Cl atoms.

Figure 14 compares NPD and TID-1 responses for a sample containing Atrazine and Chlopyrifos. Atrazine and similar Triazines are compounds which exhibit especially large TID-1 responses when the detector gas environment contains Oxygen rather than just inert Nitrogen. Like previous data on Simazine, the TID-1 response to Atrazine can be attributed to a Cl atom in a para location relative to other functionalities in its molecular structure.

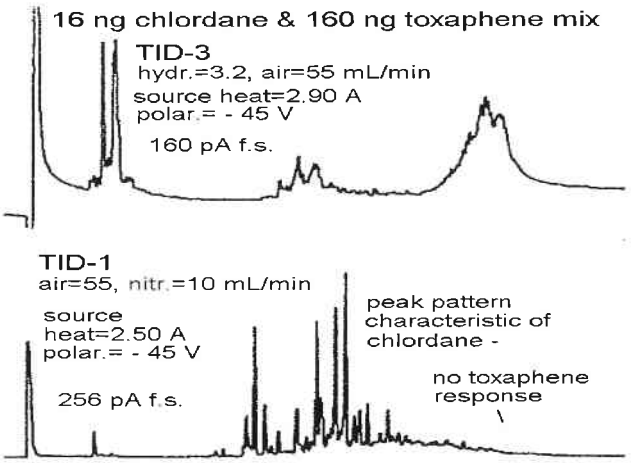


Figure 12. DET NPD/TID equipment on an HP 5890 GC.

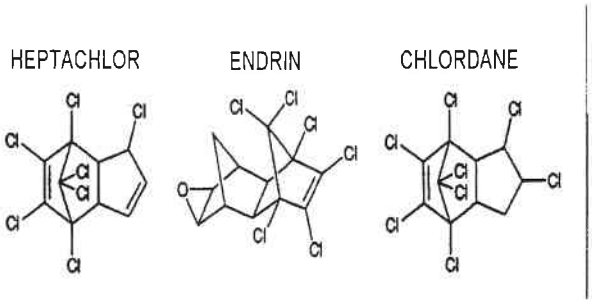


Figure 13. Molecular structures.

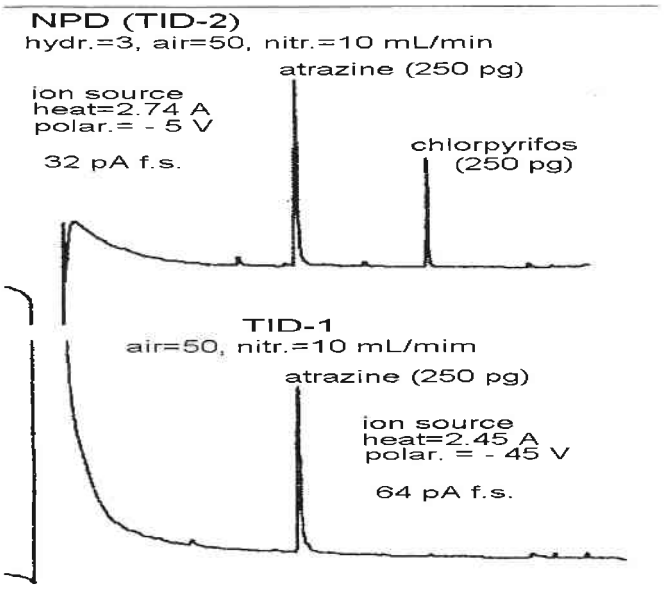


Figure 14. Agilent 6890 NPD equipment with ion sources powered by DET Current Supply.

Exceptional Selectivity for Many Oxygenated Compounds.

One of the best illustrations of the unique selectivity provided by TID-1 ionization is the analysis of Ethanol in Gasoline as shown in Figure 15. Although the magnitude of TID-1 response to Ethanol is not nearly as large as for NO_2 or Cl compounds, the selectivity is still exceptional so that Ethanol is easily detected amongst the complex Hydrocarbon matrix of Gasoline. In Figure 15, the selectivity allowed a single Nitrogen supply to be used for both GC carrier and detector gases, and a short analysis time, because there was no need to resolve the many overlapping Hydrocarbons. Figure 16 compares two different commercially available gasoline samples.

Alcohols, Aldehydes, Ketones, Esters, and Phthalates generally have a tertiary level of TID-1 response, and are best detected with a Nitrogen detector gas environment. Figure 17 shows a comparison of FID and TID-1 chromatograms for a mixture of Phthalates and Hydrocarbons. The FID detected the larger Hydrocarbon concentrations plus the Phthalates, while TID-1 detected only the Phthalates.

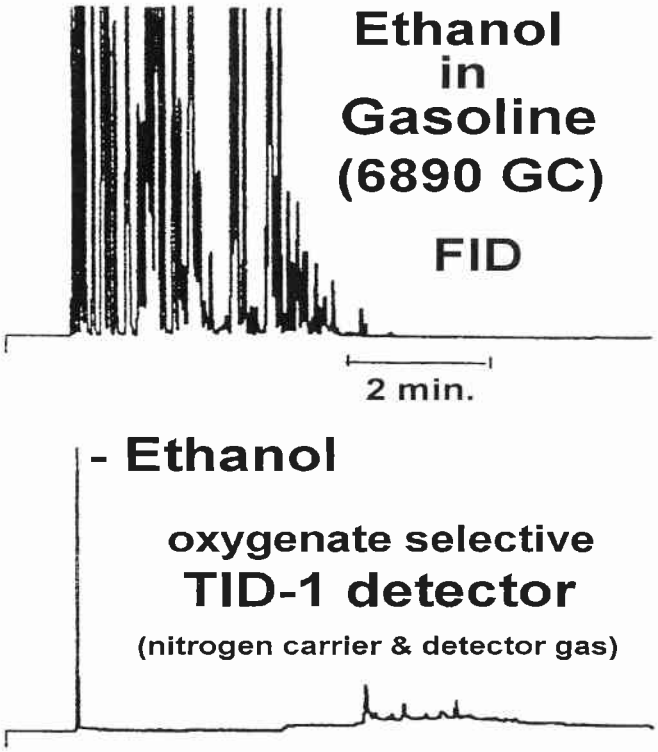


Figure 15. Gasoline analyses on an Agilent 6890 GC. TID-1 ion source installed in 6890 NPD hardware and powered with a DET Current Supply. TID signals measured with the 6890 NPD electrometer.

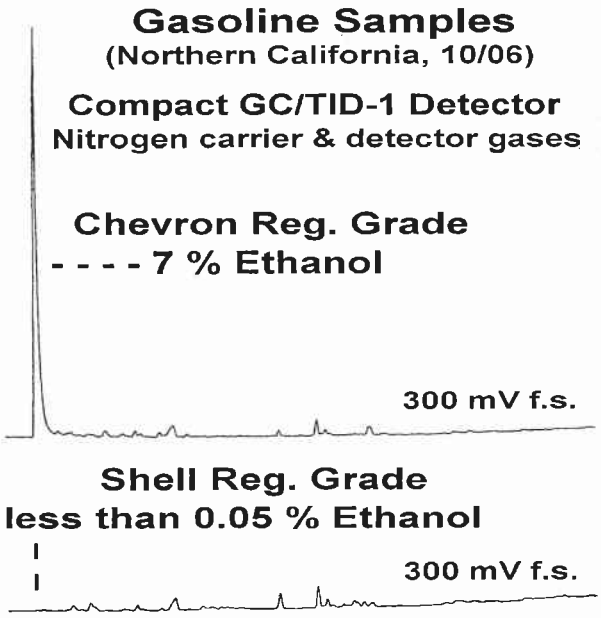


Figure 16. SRI 310 GC with DET detector & Current Supply.

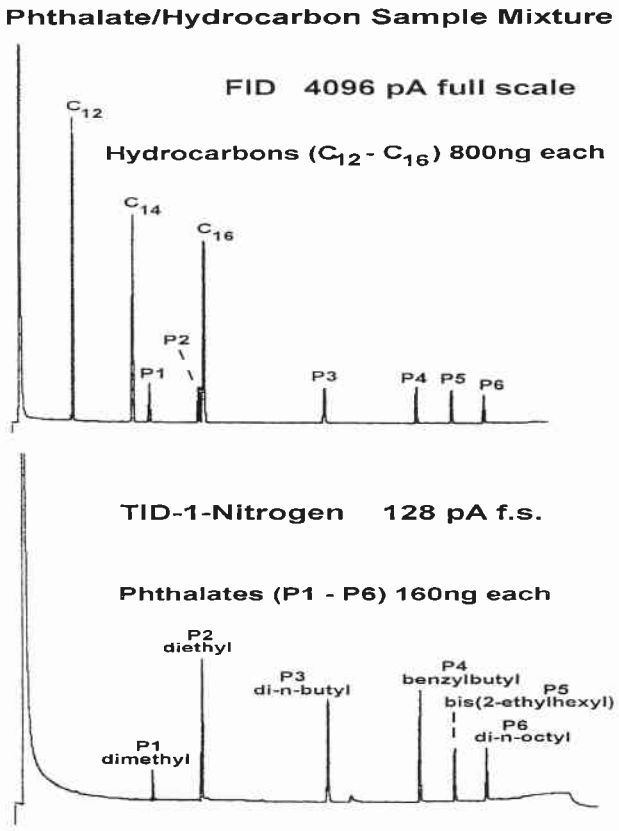


Figure 17. Agilent 6890 GC.

Among the different classes of oxygenated compounds, Ethers are not detected very well by TID-1 ionization. However, Phenols and Glycols are especially well detected with detectivites in the secondary level of TID-1 response. Figures 18 and 19 show some Phenol and Glycol responses versus Alcohols, as well as selectivity versus Hydrocarbons.

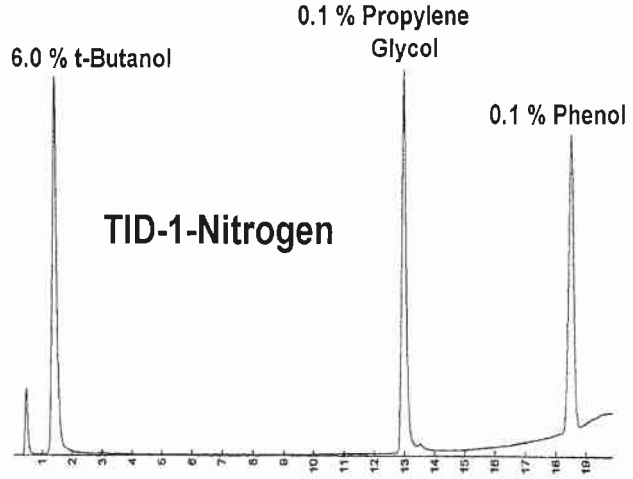


Figure 18. SRI 310 GC with DET detector & Current Supply. Response to Glycols & Phenols much larger than Alcohols.

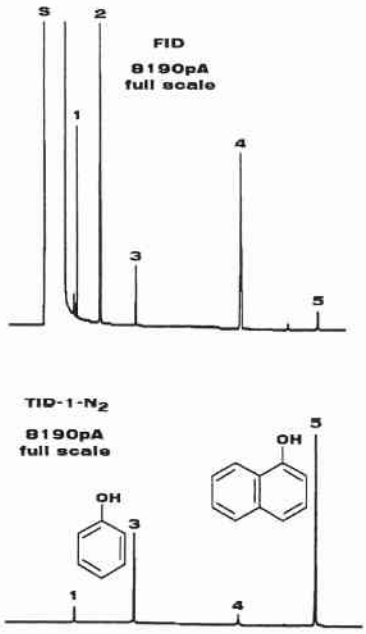


Figure 19. Agilent 6890 GC. S=benzene solvent, 1=260ppm cyclopentanol, 2=990ppm p-xylene, 3=51ppm phenol, 4=350ppm n–decanol, 5=51ppm 1-naphthol TID-1: Much larger phenol vs. alcohol responses.

Carboxylic Acids are another class of oxygenates which have much larger responses than Alcohols, and which are detectable at the secondary level of TID-1 response classification. Figure 20 compares FID and TID-1 responses for a mixture of Carboxylic Acids, Alcohols, and Hydrocarbons. It is noteworthy that TID-1 detection includes a response to Formic Acid, whereas an FID has negligible response to this compound.

In Figure 20, Air was used as the TID-1 detector gas, and this further suppressed the response to the Alcohol and Acetate components compared to what they are with a Nitrogen gas environment. An Air gas environment is useful in applying TID-1 detection to analyses of Alcoholic Beverages because it minimizes the large signal that otherwise would occur from the Ethanol content of these samples. Figure 21 compares TID-1-Air and FID chromatograms for a wine sample.

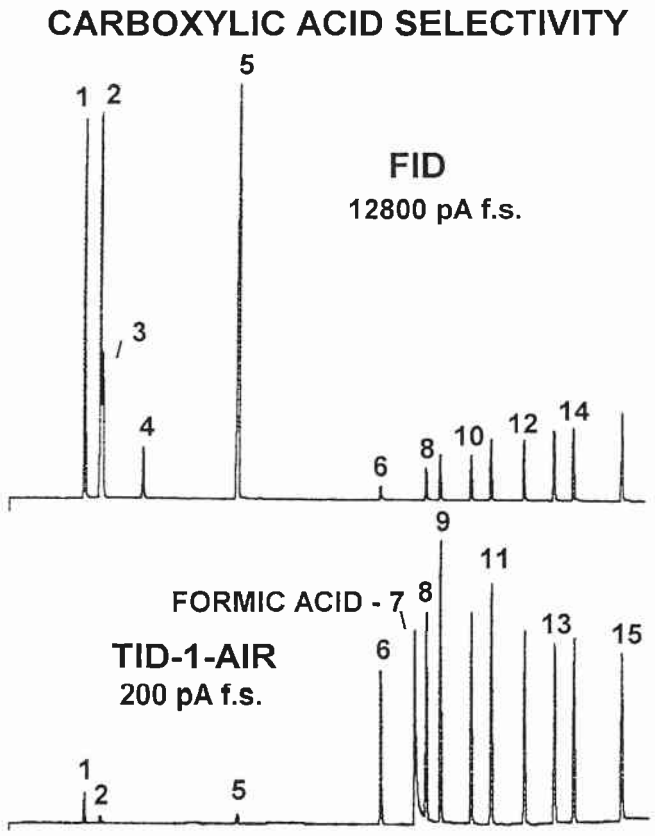


Figure 20. Agilent 6890 GC. Sample components in water. 1=ethanol (1%), 2=ethyl acetate (1%), 3=benzene (0.15%), 4=toluene (0.1%), 5=iso-pentanol (1%), 6=acetic acid (0.1%), 7=formic acid (0.1%), 8=propionic acid (0.1%), 9=iso-butyric acid (0.1%), 10=butyric acid (0.1%), 11=iso-valeric acid (0.1%), 12=n-valeric acid (0.1%) 13=iso-caproic acid (0.1%), 14=n-caproic acid (0.1%) 15=heptanoic acid (0.1%).

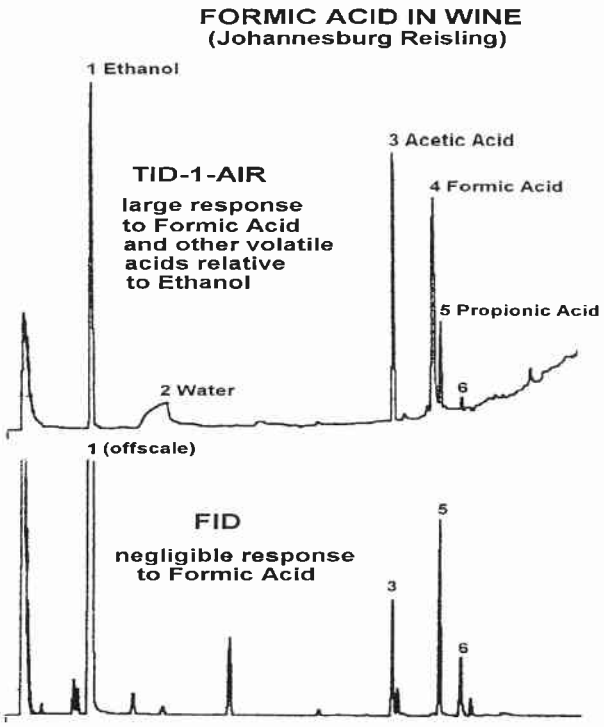


Figure 21. Varian 3800 GC. 0.4µL wine injected.

Figure 22 shows another comparison of TID-1-Air and FID chromatograms for a wine sample. The TID-1 chromatogram is displayed at an enhanced sensitivity in order to show some of the minor peaks. One component of interest in this sample was Diacetyl (peak 5). The Air environment in the TID-1 detector suppressed the large Ethanol p eak sufficiently to allow Diacetyl to be a well defined peak in the TID-1 chromatogram. Compared to the FID, the TID-1-Air chromatogram exhibited suppressed signals for Acetaldehyde, Ethyl Acetate, and all the Alcohols, but a significant response to Water (peak7) and very large signals for the Volatile Acids. The TID-1 chromatogram also revealed the significant presence of Formic Acid in this sample. Among the many thousands of reports on wine analyses, very few mention Formic Acid. It appears from data like Figures 21 and 22 that this strong acid has been present in wines, but it has not been detected because the FID was used for most analyses. This is a good example of how the unique capabilities of TID-1 surface ionization often reveal sample constituents undetected by other means.

Vanillin is another compound often found in wines and other food, flavor, and fragrance samples. TID-1 ionization in a Nitrogen gas environment has an exceptionally large sensitivity to Vanillin. This is demonstrated in Figure 23. In this analysis of an imitation Vanilla extract, the TID-1 and FID data were displayed at the same full scale sensitivity, yet the TID-1 signal for Vanillin was well offscale. Figure 24 demonstrates a similar high sensitivity to a trace Vanillin constituent of a Fragrance sample.

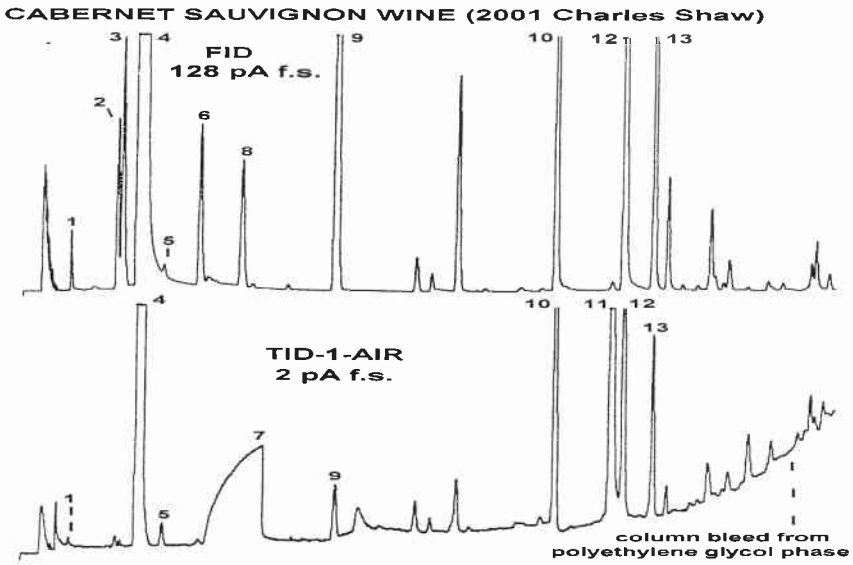


Figure 22. Agilent 6890 GC. 0.7µL wine injected. 1=acetaldehyde, 2=ethyl acetate, 3=methanol, 4=ethanol, 5=diacetyl, 6=n-propanol, 7=water, 8=iso-butanol, 9=iso/active amyl alcohols, 10=acetic acid, 11=formic acid, 12=propionic acid, 13=isobutyric acid.

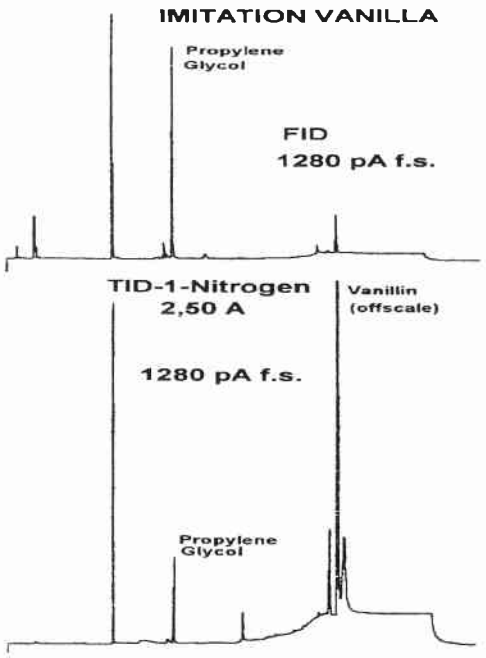


Figure 23. Varian 3800 GC. 0.7µL of imitation Vanilla extract diluted 1:20 in water.

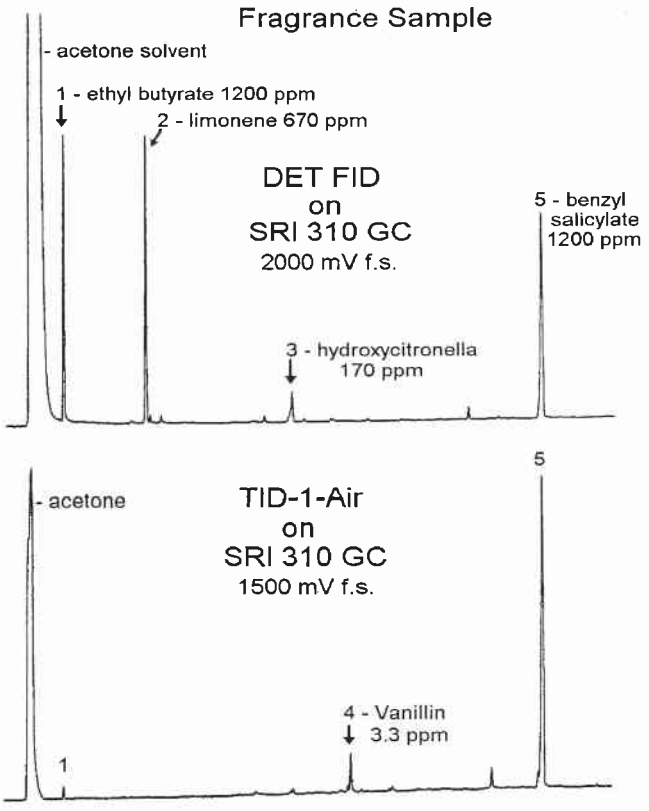


Figure 24. SRI GC with DET detector & Current Supply.

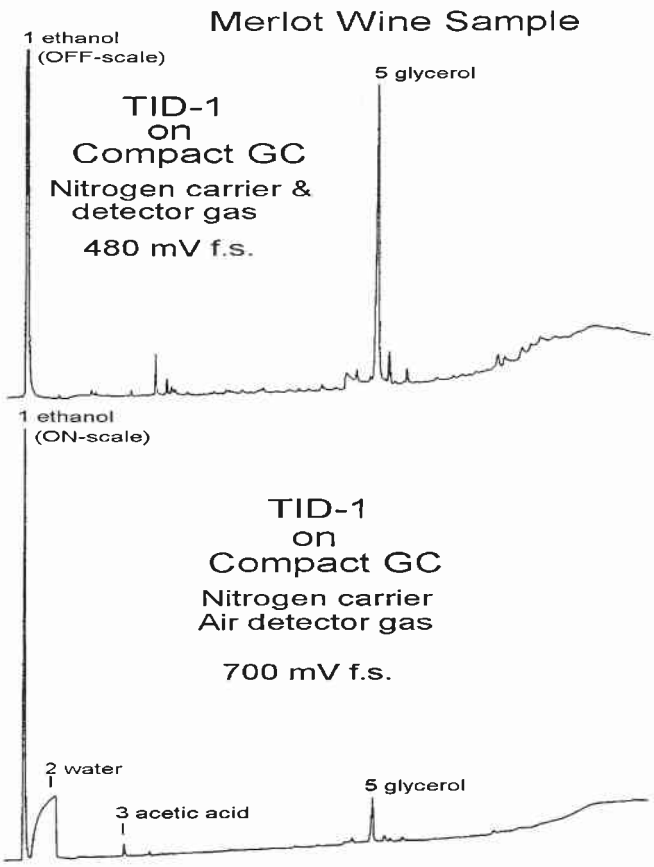


Figure 25. SRI GC with DET detector & Current Supply. 0.3µL direct injection of Merlot wine.

Glycerol is another major constituent of wines, and it has an excellent TID-1 response when Nitrogen is used as the detector gas environment. Figure 25 demonstrates this in an analysis of a Merlot wine sample. Because Glycerol is such a prominent peak in the TID-1 chromatogram, a simple system using a single Nitrogen supply suffices for both GC carrier and detector gases. Figure 25 also demonstrates that the relative magnitude of Glycerol is diminished when Air is used in place of Nitrogen for the detector gas.

The bottom chromatogram in Figure 25, as well as several earlier wine chromatograms, demonstrate that Water is detected by TID-1 ionization when the TID-1 surface is operated in an oxidizing gas environment. TID-1 sensitivity to Water is in the tertiary level of response, which correlates to about a 1 ppm detection limit. Figures 26, 27, and 28 illustrate TID-1-Air detection of trace Water in Solvents, Ambient Air, and a Naphtha Standard.

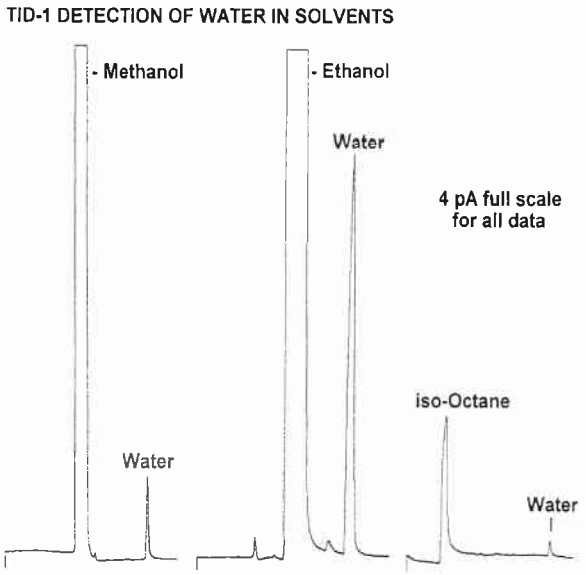


Figure 26. Agilent 6890 GC. Residual water in solvents. 2.2µL injections of each solvent. TID-1 ion source powered by DET Current Supply. Detector gases: Air=50, N_2 =10 mL/min.

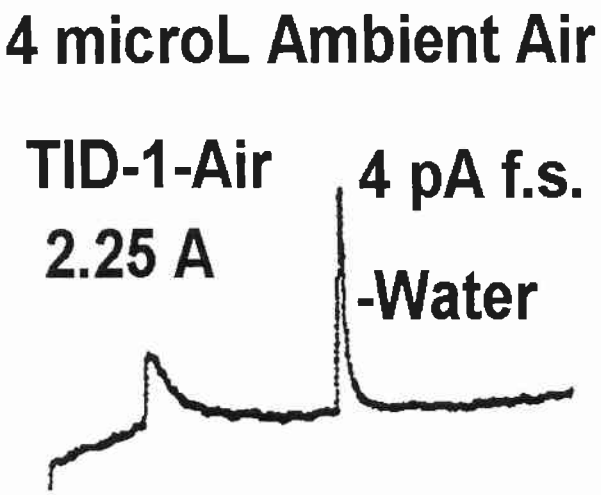


Figure 27. Agilent 6890 GC. 4 µL of Ambient Air injected via a gas tight syringe. Detector gases: Air=55, N_2 =5 mL/min.

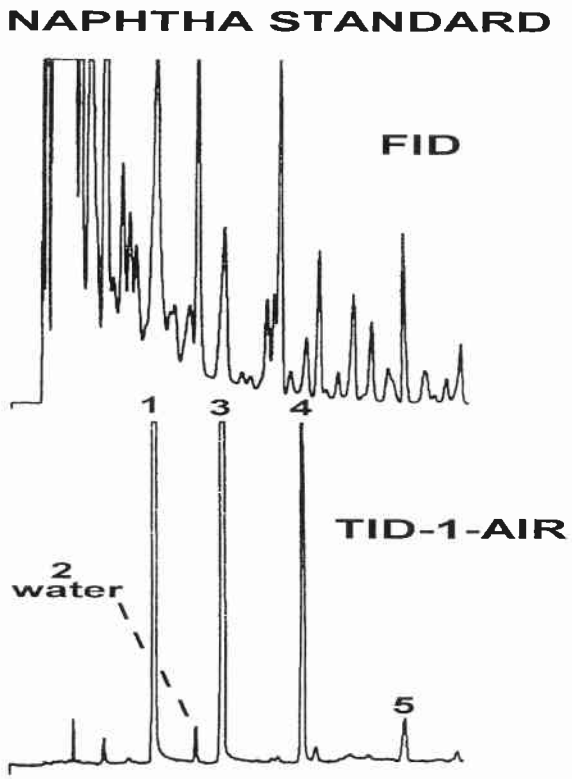


Figure 28. Agilent 6890 GC. 0.4 µL injection of a Naphtha standard. Detector gases for TID: Air=50, N_2 =10 mL/min.

An earlier chromatogram illustrating the analysis of Ethanol in Gasoline demonstrated how TID-1 surface ionization can selectively detect an Oxygenated component amongst a complex Hydrocarbon matrix. The fact that TID-1 responses to some classes of Oxygenates are substantially larger than others can similarly be useful in analyses of samples involving complex Oxygenated matrices. Such an analysis is illustrated in Figure 29 for an Essential Oil matrix containing the antioxidants BHA and BHT. Using an detector gas environment composed of Oxygen, TID-1 ionization allowed the detection of BHA and BHT which were otherwise hopelessly buried amidst the many peaks of the FID chromatogram.

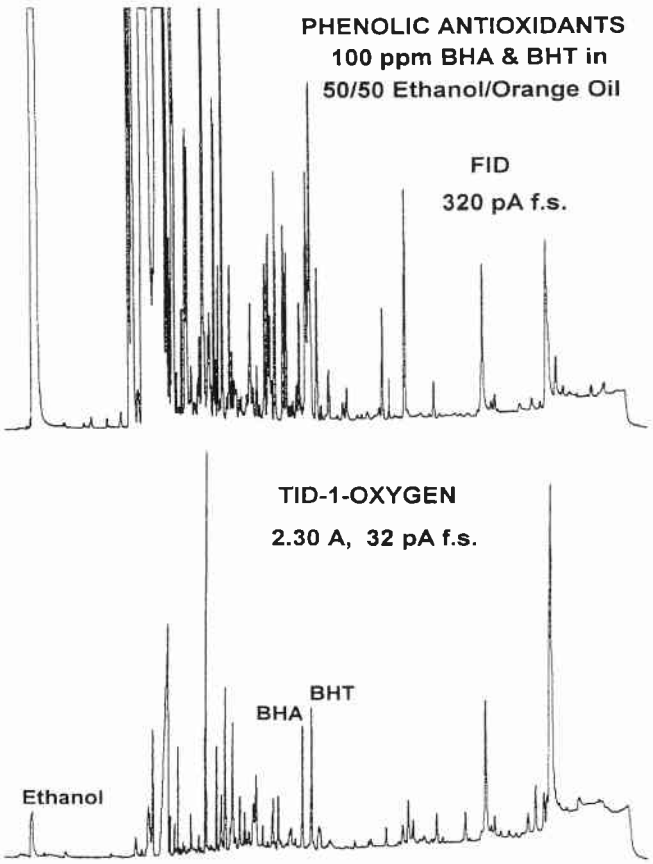


Figure 29. 0.7µL injection of 50/50 mixture Ethanol/Orange Oil with 100 ppm each of BHA & BHT.

For a detector like TID-1 which is selective and sensitive to oxygenated compounds, another area of application is the detection of products of oxidative degradation of various substances. This situation is illustrated in Figure 30 in the comparison of TID-1 responses for used versus new Motor Oil samples. Chromatographic peaks that appear larger and larger as the motor oil is used are easily detected by the TID-1 detector. Monitoring of Motor Oil changes with time is readily accomplished by obtaining a drop of oil from an automobile engine dip stick, then diluting it appropriately to achieve a sample viscosity allowing easy GC injection. TID-1 detection with a detector gas environment of Nitrogen then reveals the presence of oil degradation products.

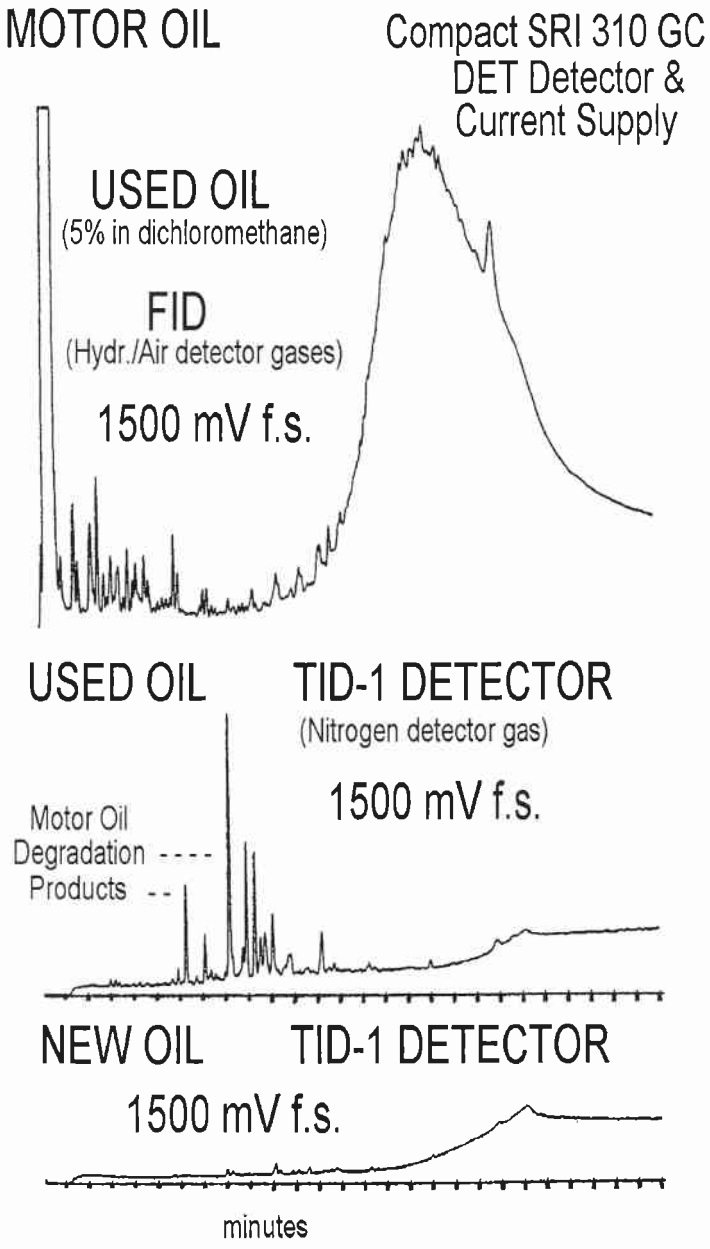


Figure 30. 0.8µL injections of 5% oil in dichloromethane. 15m x 0.32mm x 3.0µm AT-1 fused silica column with Helium carrier gas and Nitrogen detector gas for the TID-1 mode.

Unique Selectivity for Certain Drug Compounds.
Figures 31 and 32 compare NPD and TID-1 responses for mixtures of common drug compounds. All the compounds analyzed contained N atoms and exhibited good NPD responses, but TID-1 was much more selective to just the Heroin and Diazepam components in the samples.

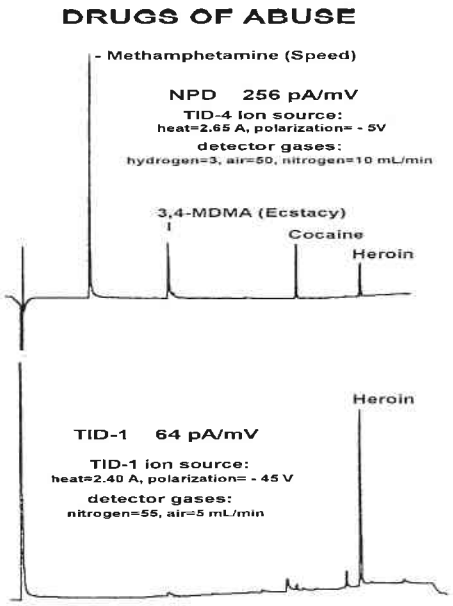


Figure 31. Agilent 6890 GC. 5ng each drug.

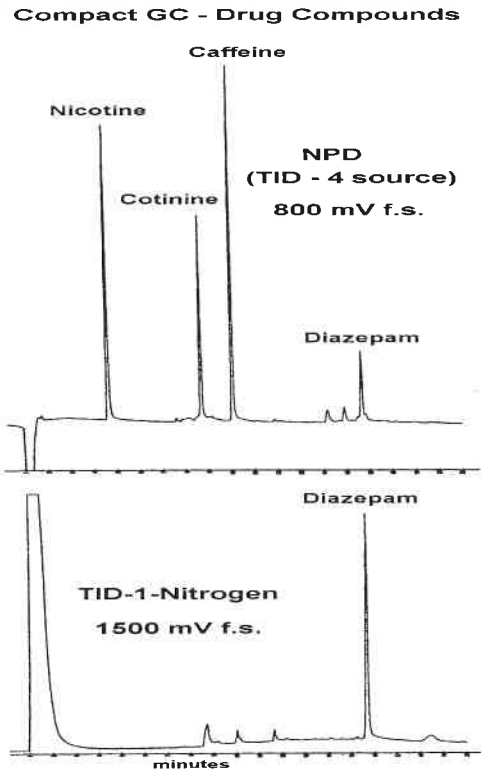


Figure 32. SRI 310 GC. 9.6ng each drug.

Unique Selectivity for the Pyrrole vs. Pyridine Functional Group and for the Five Member Hydrocarbon Compound Flourene vs. Other PAH Compounds.
Figure 33 compares FID, NPD, and TID-1 chromatograms for a mixture of polynuclear Hydrocarbons and Nitrogen compounds. Whereas the NPD responded to all the N compounds, TID-1 selectively detected only the Pyrrole heterocycles, Indole and Carbazole, but not the Pyridine heterocycle Quinoline. TID-1 also exibited a lower level of response to Indene and Fluorene, the five member ring Hydrocarbon analogs of Indole and Carbazole. Figure 34 further illustrates the selective detection of Fluorene amidst a mixture of other PAH compounds.

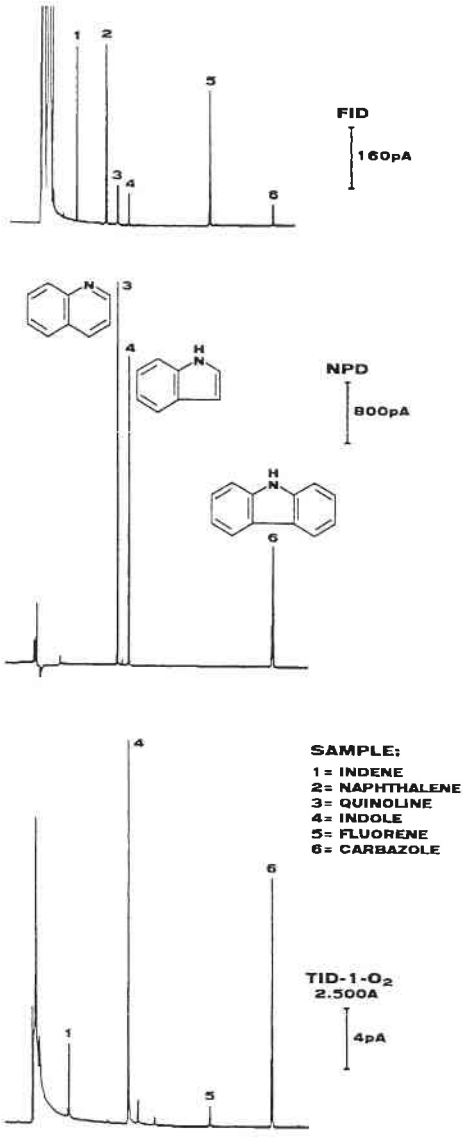


Figure 33. Varian 3800 GC. 1=320ng indene, 2=320ng naphthalene, 3=78ng quinoline, 4=66ng indole, 5=320 ng fluorene, 6=66ng carbazole.

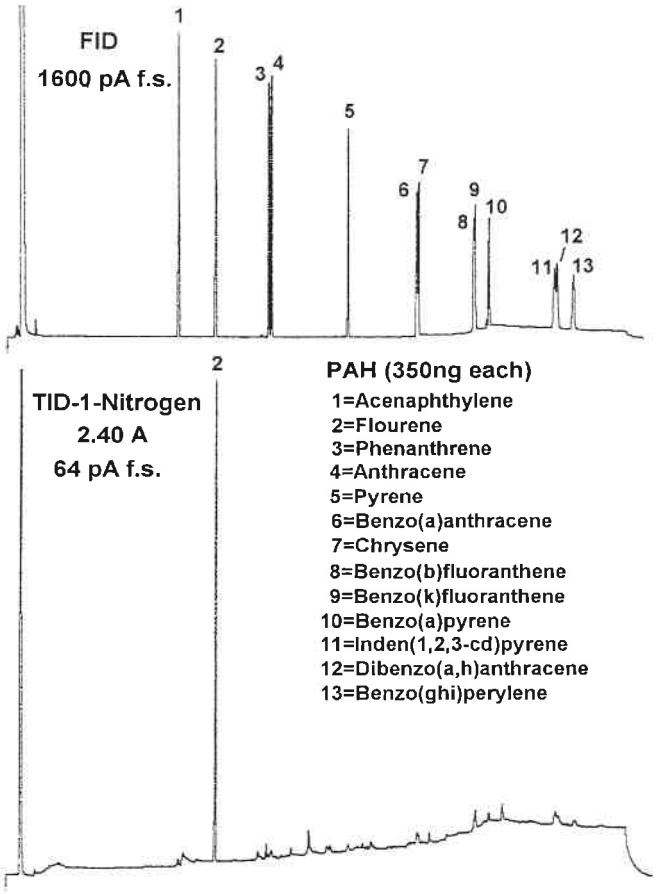


Figure 34. Agilent 6890 GC.

Sensitivity to Some Aroma Compounds - Anisole, 2,4,6-Trichloroanisole, and Allyl Isothiocyanate (Oil of Mustard).

Figures 35 and 36 illustrate TID-1 responses to Anisole, 2,4,6-Trichloranisole, and Allyl Isothiocyanate. Among these 3 compounds, Anisole was the least responsive to TID-1 detection. By comparison, 2,4,6-Trichloroanisole was 180 times more responsive on a gram per gram basis, while Allyl Isothiocyanate was 1300 times more responsive than Anisole.

It was mentioned earlier in this report that a TID-1 detector is non destructive. Consequently, aromas characteristic of different sample constituents can be sensed as they elute at their respective retention times from the detector exit port, even if the detector's ionization process does not produce a measurable signal.

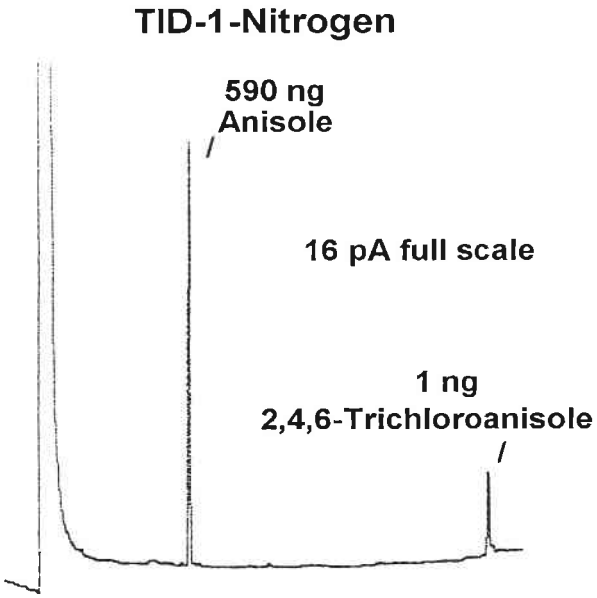


Figure 35. Agilent 6890 GC.

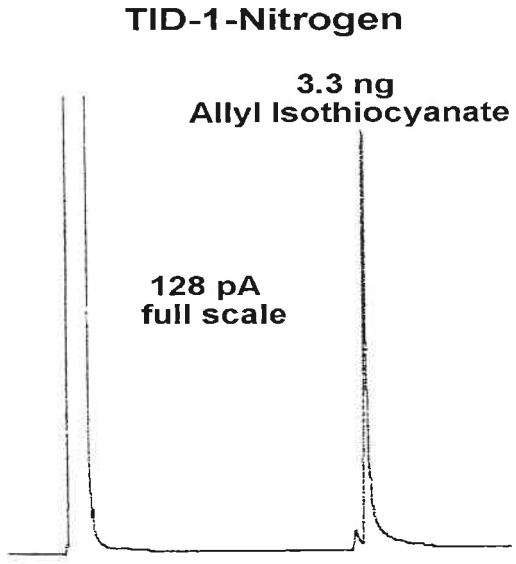


Figure 36. Agilent 6890 GC. Large TID-1 response to Allyl Isothiocyanate.

Macro Responses of the TID-1 Detector - Selectivity for the CH_2 Functional Group in High Concentrations of Hydrocarbons.

Figure 37 compares FID and TID-1 chromatograms for a sample containing a mixture of high concentrations of Aromatic, Linear, and Branched Chain Hydrocarbons, plus a minor concentration of Ethanol. In contrast to the FID which responded to all the Hydrocarbons, the TID-1 surface ionized only the Linear Chain Hydrocarbons when operated in a detector gas environment of Oxygen, and only the Branched Chain Hydrocarbons plus Ethanol when operated in a Nitrogen environment. In neither gas environment was there a TID-1 response to the sample's Aromatic Hydrocarbons.

The full scale sensitivities for the chromatograms in Figure 37 show that for this sample, TID-1 ionization in an Oxygen environment produced much larger signal magnitudes (i.e., larger ionization efficiency) than TID-1 ionization in Nitrogen. At the 2.50 A source heating current and -45 V source polarization used for these data, the TID-1-O_2 ionization efficiencies for C_{12}, C_{14}, and C_{16} were within an order of magnitude of the FID signals. TID signals can be increased further by supplying higher heating currents, but at the risk of shortening the operating life of the ion source. Note also that TID-1-N_2 detection revealed an impurity component "U" that was not evident in either of the other 2 chromatograms.

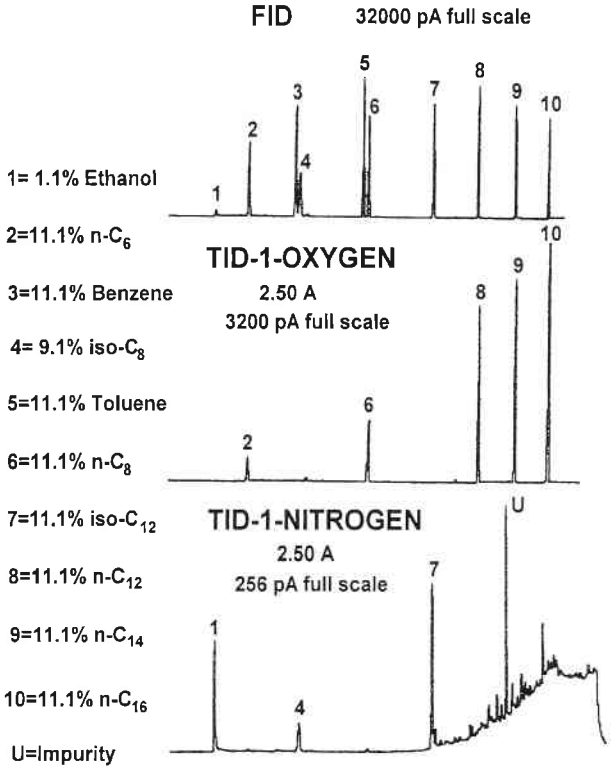


Figure 37. Varian 3800 GC. 0.1µL sample injection.

Figure 38 shows the molecular structures of the C_8 and C_{12} constituents of the Figure 37 sample, and it is instructive to correlate these with the TID-1 responses. In the Nitrogen environment, TID-1 detection responded to iso-C_8 and iso-C_{12}, but not their linear chain counterparts, and the iso-C_{12} signal was significantly larger than that of iso-C_8. Considering the structures in Figure 38, the data indicate that the magnitude of TID-1-N_2 ionization is related to the number of branched CH_3 functional groups in the sample molecule. The linear chain compounds had no branched CH_3 groups, and therefore no response.

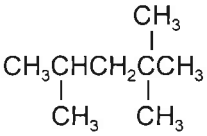
In contrast, in the Oxygen environment, the linear C_8 and C_{12}, as well as C_6, C_{14}, and C_{16}, were selectively ionized with signal magnitudes increasing as the number of methylene (CH_2) functional groups in the sample molecules increased. The branched C_8 and C_{12} constituents of the sample contained very few CH_2 in their structures, and therefore had a negligible TID-1-O_2 response.

Figures 39 and 40 provide further illustrations of the correlation of TID-1-O_2 responses with the number of CH_2 functional groups for equal mixtures of Alkanes (Figure 39) and Alkenes (Figure 40). For Alkane and Alkene molecules with comparable numbers of CH_2 groups, the Alkane response was consistently higher.

n –OCTANE

$CH_3(CH_2)_6CH_3$

iso-OCTANE
(2,2,4-TRIMETHYLPENTANE)



n–DODECANE

$CH_3(CH_2)_{10}CH_3$

iso-DODECANE
(2,2,4,6,6-PENTAMETHYLHEPTANE)

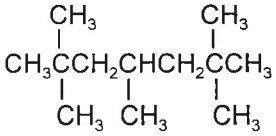


Figure 38. Structures of Octane and Dodecane compounds in Figure 37 chromatograms.

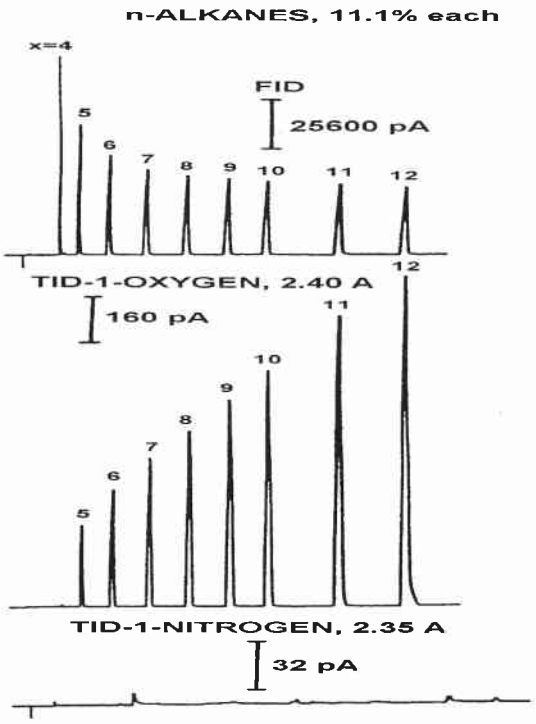


Figure 39. n-Alkane sample, $CH_3(CH_2)_XCH_3$, X= number of Methylene groups (CH_2) in the molecule. 0.6µL injected.

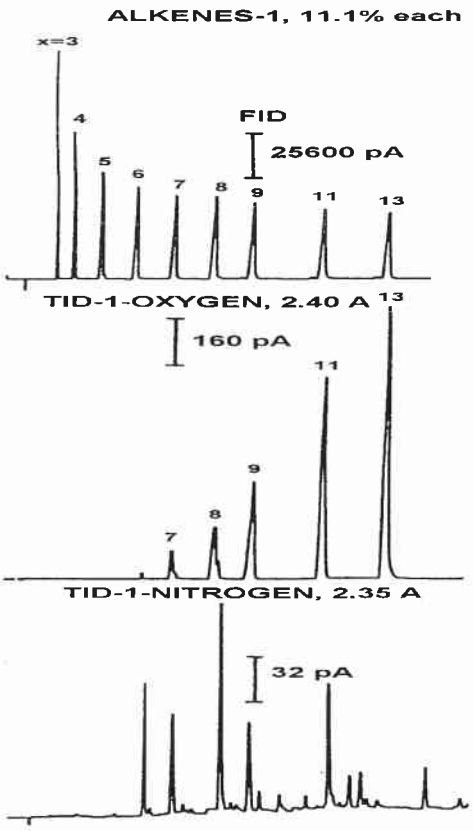


Figure 40. Alkene-1 sample, $CH_3(CH_2)_XCH=CH_2$.

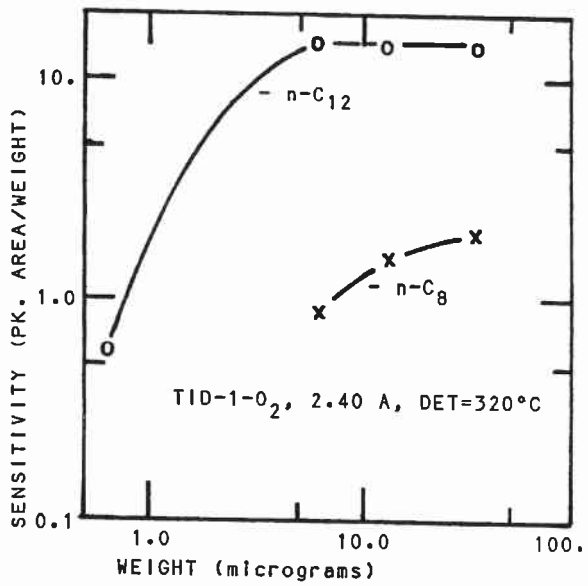


Figure 41. Graph of peak area sensitivity versus sample weight TID-1-O_2 detection.

Both Figures 39 and 40 include TID-1-N_2 chromatograms of the Alkane and Alkene samples. The Alkane standards used were relatively free of heteroatom impurities that would produce TID-1-N_2 responses. However, the corresponding TID-1-N_2 chromatogram of the Alkene mixture revealed numerous impurity constituents that were not evident in the FID chromatogram, and only partly evident in the TID-1-O_2 chromatogram.

Figure 41 shows a plot of TID-1-O_2 sensitivity versus sample weight where the sensitivity to n-C_{12} decreased rapidly below a sample weight of 5 µg. This concentration threshold of response indicated that the ionization produced was the result of the mutual interaction of O_2 , the hot (i.e., 400 - 500°C) TID-1 surface, and two or more C_{12} molecules. In effect, the onset of detectable ionization for straight chain CH_2 functional groups can be likened to a microscopic ignition process each time a large concentration of a Hydrocarbon elutes from the GC column. On a graph such as Figure 41, the threshold curve exhibited by C_{12}, moves up and to the left for molecules with greater numbers of CH_2 groups, and down and toward the right for molecules with fewer CH_2 groups. Similarly, the C_{12} curve moves up and toward the left with

larger heating currents to the TID-1 ion source, and down and toward the right with lower heating currents. Also, if the concentration of O_2 in the detector volume is decreased by using Air instead of Oxygen, then the C_{12} threshold curve moves down and toward the right (i.e, threshold at higher sample weights and lower sensitivity).

Figure 42 compares FID, TID-1-O_2 and TID-1-N_2 chromatograms for a Naphtha standard. The TID chromatograms demonstrate selectivity for the linear Alkanes present in the sample.

Figure 43 illustrates how high concentrations of linear Alkanes can affect TID-1-Air chromatograms. In the top chromatogram, at the 800 ng level the Alkane peaks appear prominently along with the lower concentrations of Phthalates. However, when that sample was diluted by a factor of 10, the Alkane peaks were virtually non-existent compared to the Phthalates. Figure 44 shows a graph of sensitivity versus sample weight illustrating the threshold drop in response for C_{16} in comparison to the Phthalate response.

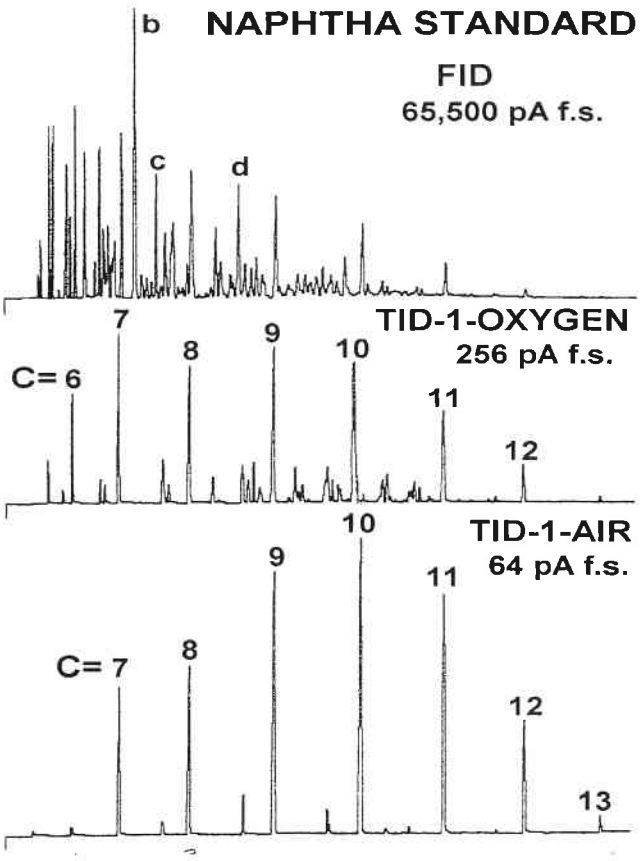


Figure 42. Agilent 6890 GC. 0.1µL injected. C=carbon number of linear alkanes.

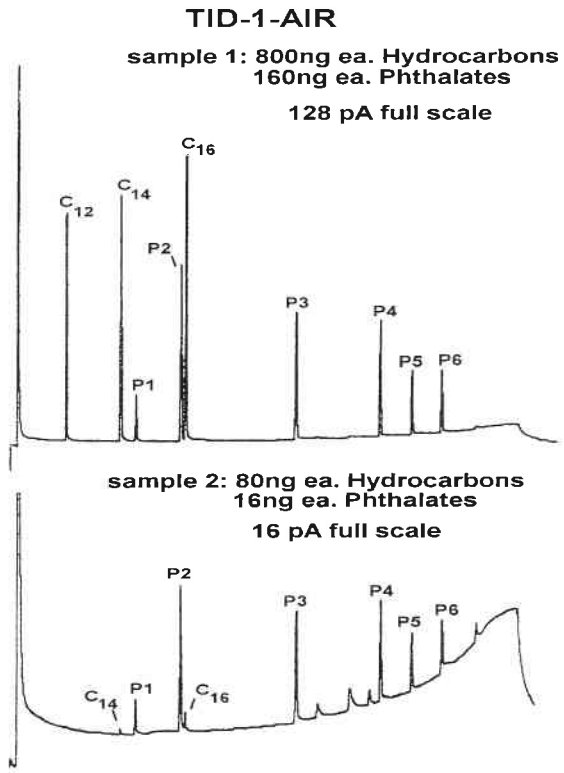


Figure 43. n–Alkanes: C_{12}, C_{14}, C_{16} .
Phthalates: P1=dimethyl, P2=diethyl, P3=di-n-butyl, P4=benzylbutyl, P5=bis(2-ethylhexyl), P6=di-n-octyl.

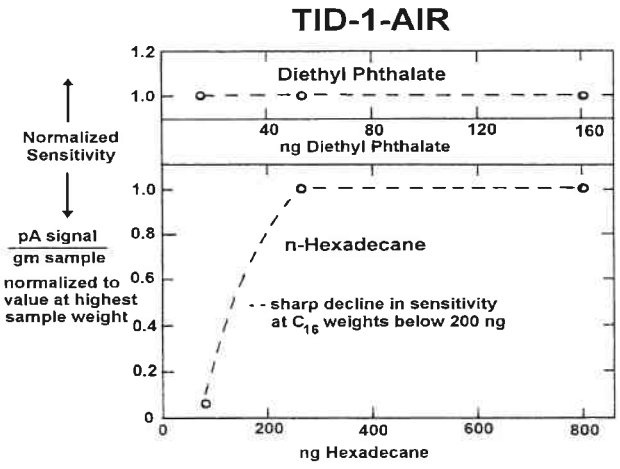


Figure 44. Graph of normalized sensitivity vs sample weight.

Sensitivity = pA of peak height signal divided by sample weight. Sensitivity data normalized by dividing the sensitivity corresponding to the data point at the highest sample weight. Linearity on this type of plot is indicated by a horizontal line.

Accessing TID-1 Detection on Different Brand GC Models.
DET manufactures TID-1 ion sources in 2 standard configurations. A 3/4 inch Hexagonal flange mounting fits NPD structures manufactured by Agilent, as well as all DET detector structures, and a 1/4 inch Tube mounting is used by Thermo Fisher Scientific and SRI Instruments in NPD structures that they manufacture. DET's part number for a hexagonal flanged TID-1 ion source is 010-901-00 (with connector) or 010-901-01 (without connector). DET's part number for the 1/4 inch tube TID-1 ion source is 110-901-00 (with connector) or 110-901-01 (without connector).

Agilent 6890/7890 GC models. Replace the NPD ion source with a TID-1 source (DET part 010-901-00) and change the detector gas environment from Hydrogen/Air to Nitrogen, Air, or some combination. The Agilent NPD electrometer works fine for measuring TID-1 signals. The Agilent NPD Bead Voltage supply can be used to power TID-1 ion sources and provide TID-1 selectivity. However, much better TID-1 sensitivity is achieved by powering the ion source with a higher - 45 V polarization available from a DET Current Supply (DET part 001-901-01). Figures 45 and 46 illustrate this for the selective detection of the NO_2 group in Methyl Parathion. Figure 45 demonstrates the Methyl Parathion sensitivity and selectivity achieved using a DET supply to power the ion source, and Figure 46 illustrates the smaller magnitude signals obtained when the ion source is powered by the Agilent Bead Voltage. In addition to a selection of polarization voltages, the stand-alone DET supply provides a preferred Constant Current heating for ion sources in all modes of detection. By contrast, the Agilent NPD Bead Voltage provides a Constant Voltage type heating which is not as stable as Constant Current power for supplying electrical current through the ion source's wire core.

Thermo Fisher Scientific GC models. DET supplies Thermo with NPD and TID-1 ion sources in the standard 1/4 inch tube mounting without an electrical connector. Thermo trims the DET parts to a shorter length, and adds an electrical connector of their own design. A TID-1 coated ion source is identified by Thermo's part number 465 002 50, and described as " TS-1 source for E NS mode". Thermo's NPD electronics provide a Constant

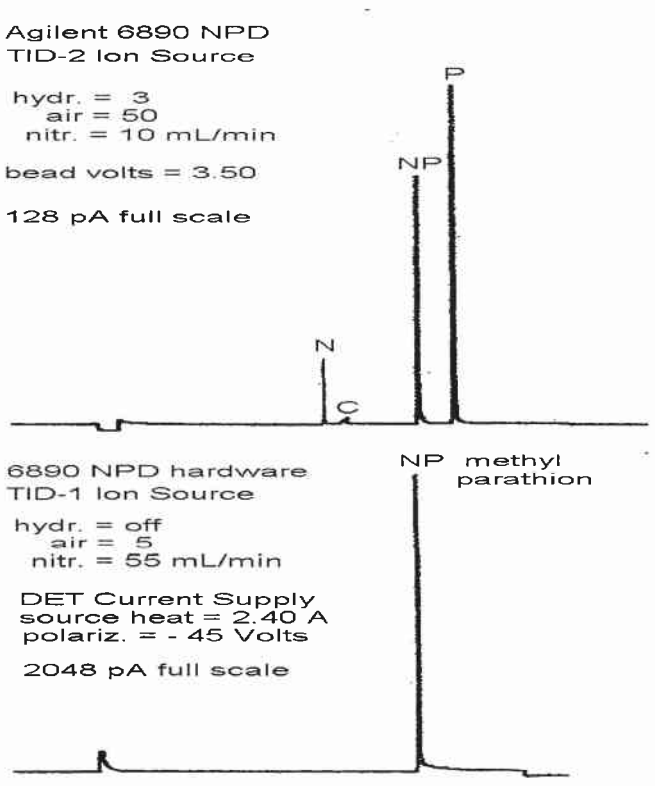


Figure 45. Comparison of NPD and TID-1 modes. Agilent 6890 with DET Current Supply. N=2ng azobenzene, C=4000ng n-C_{17} NP=2ng methyl parathion,P=4ng malathion.

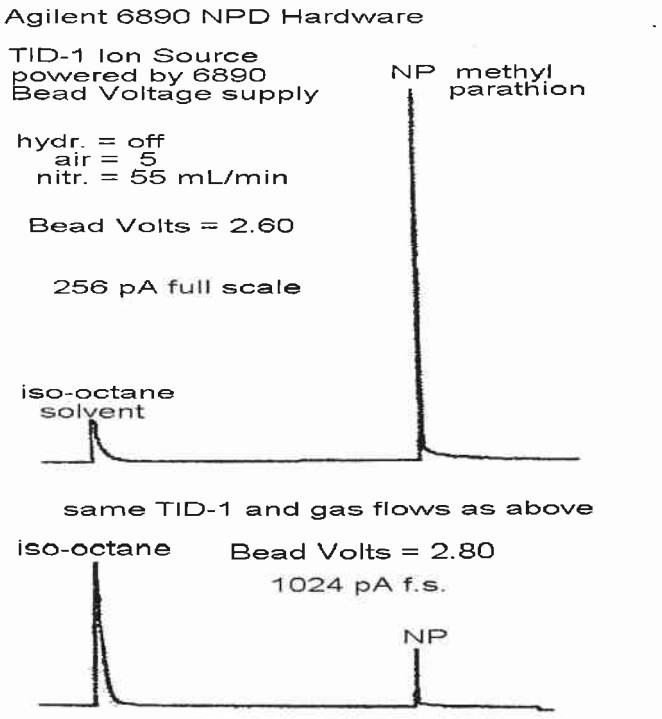


Figure 46. Repeat of the TID-1 analysis of Figure 45 except Agilent 6890 NPD Bead Voltage used to power the ion source instead of the DET supply. Higher Bead Voltage of 2.80 V did not improve methyl parathion sensitivity and decreased selectivity versus iso-octane solvent.

Current heating for the ion source and have an adjustable polarization voltage for optimum sensitivity in all detection modes. The detector hardware configuration on Thermo GC models differs from that on Agilent or DET equipment in that the ion source in inserted from the side and the collector electrode is downstream rather than the concentric cylinder configuration depicted in Figure 1.

SRI Instruments GC Models. DET supplies SRI with NPD and TID-1 ion sources in the standard 1/4 inch tube mounting without a connector for use in SRI's detector hardware. The TID-1 mode of detection is described in SRI nomenclature as simply "TID - Thermionic Ionization Detection". SRI equipment includes a power supply and electrometer for use with the NPD or TID modes. As an alternative to SRI's parts, DET also provides detector hardware (DET part 050-864-98) that mounts onto a heated FID type detector base on the SRI GC models, and that uses the standard hexagonal flanged ion sources like those used on Agilent GC models. DET's hardware provides a concentric cylinder detector configuration such as depicted in Figure 1, for improved stream-lined gas flow and optimum ion collection. A DET Current Supply is also available for use with the SRI GC to provide finer control of the heating current and polarizations used in both NPD and TID-1 modes of detection.

Varian 3800 GC. DET manufactures a detector structure (DET part 010-860-20) that mounts onto an existing FID or TSD (NPD) base on the Varian GC, and uses DET's standard hexagonal flanged ion sources. Like the Agilent situation, TID-1 detection is achieved by supplying the appropriate gases through the detector gas lines. Varian's TSD power supply/electrometer module (Varian part # 0392507001) provides a Constant Current heating power and low polarization voltage that can be used for NPD or TID-1 detection, plus a negative ion electrometer for signal measurement. However, like the Agilent equipment, a stand-alone DET Current Supply substituted for Varian's power supply provides higher polarization voltages for optimum TID-1 sensitivity.

HP 5890 GC . DET manufactures a detector structure (DET part 040-862-12) that mounts onto a 5890 FID or NPD detector base, and uses DET's standard hexagonal flanged ion sources. The DET Current Supply is required to power the ion sources, and a stand-alone electrometer such as a Keithley Model 6485 Picoammeter is required to measure detector signals.

Summary Examples of Compounds in Different Response Categories of Selective TID-1 Ionization.

Primary response. Nitro compounds - 2,4-Dinitrotoluene, TNT, 4-Nitrophenol, Methyl Parathion, Aldehyde-DNPH. Halogenated Compounds - Heptachlor, Dieldrin, Endrin , Pentachlorophenol.

Secondary response. Most Nitro compounds not included in primary response. Most halogenates not included in primary response. Atrazine and other Triazines with an Air environment. Oxygenates like Phenols, Glycols, Carboxylic Acids, Vanillin, Methyl Salicylate.

Tertiary response. Most Oxygenates not included in secondary response. Nitrogen heterocycles containing the Pyrrole functional group. Water with an Air environment.

Macro response. Methylene (CH_2) functional groups with an oxidizing gas environment.