DET REPORT

NO.73 NOVEMBER 2016

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1.) NPD & TID-10 SELECTIVE DETECTION OF FENTANYL, HEROIN, AND OTHER OPIATES AND DRUGS OF ABUSE.

The narcotic Fentanyl has received a lot of news media attention in recent years. It is the compound reported to be responsible for the death of the popular entertainer "Prince", and its unsuspected combination with street Heroin has contributed to overdose deaths of many other drug users. In some parts of the United States, drug deaths associated with Fentanyl and Heroin are regarded to be near epidemic levels.

Most drugs of abuse contain Nitrogen atoms, and are amenable to selective GC detection using a Nitrogen Phosphorus Detector (NPD). DET's TID-4 White Ceramic ion source has a surface coating specifically formulated to give the best possible N response for an NPD. A standard configuration of this ion source is mounting on a hexagonal shaped flange that is compatible with NPD hardware on Agilent 6890/7890 and Thermo Trace 1300 GC models. This same ion source mounting is also used in all DET Retrofit detector hardware designed to custom fit several other GC models.

DET's main business is manufacturing electrically heated ionizing elements made of ceramic materials, and developments over the years have provided a family of ceramic ion sources with different catalytic and ionizing activity for use in selective detection of compounds other than just NP compounds. This section of this report provides comparisons of NPD(TID-4) detection versus TID-10 selective detection for assorted drugs of abuse.

Figure 1 shows NPD analysis of a sample prepared from purchased Heroin and Fentanyl standards. The Heroin standard, in this case, came as a solution in Acetonitrile, so NPD analysis was complicated by the requirement to detect low level N compounds in a solvent also containing a large quantity of an N compound. The top chromatogram in Figure 1 illustrated the analysis problem, while the bottom chromatogram showed that the large solvent peak could be eliminated by turning off the NP chemistry during solvent elution. This was accomplished by manually reducing the ion source heating current while the solvent passed through the detector. The present data were generated on an Agilent NPD GC supplemented by a stand-alone Current Supply to power the ion source. For a similar situation with a Thermo NPD GC, ion source power can be turned On/Off automatically as a timed event on the GC.

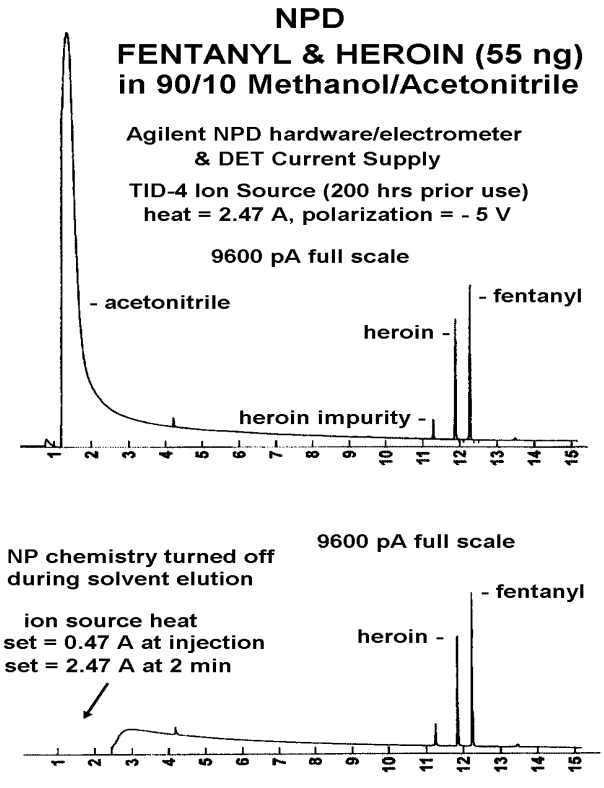

Figure 1. column: 30m x 0.32mm x 0.25µm DB-5ms, He=4mL/min, 100 - 300degC at 15degC/min.
detector gases: H2=3, Air=60, N2 make up=10mL/min

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Figure 2 shows the same Fentanyl and Heroin sample analyzed with a TID-10 mode versus the NPD mode. Compared to a TID-4 NPD ion source, a TID-10 ceramic ion source is a more catalytically active surface having a lower work function for the emission of negative electrical charge. Furthermore, TID-10 is intended for operation in a non-destructive detector gas environment of Nitrogen rather than the ignited Hydrogen - Air environment required for NP selectivity. A further distinction is that TID-10 detection provides its best signal to noise responses with ion source to collector polarization voltages of - 45 V or larger, whereas optimum NP response is obtained at a low polarization of - 5 V or lower. This is the main reason why data presented in this report were obtained using a stand-alone DET Current Supply substituted for the Bead Voltage supply that exists with Agilent NPD electronics. The DET supply provides a polarization voltage selection of - 5, - 15, or - 45 V for optimum response in all detection modes, whereas Agilent's Bead Voltage is fixed at a polarization of - 4.4 V which is best only for NP detection.

In the chromatograms of Figure 2, TID-10 provided good response to Heroin and a 6-Acetylmorphine impurity in the purchased Heroin, but had a much suppressed response for Fentanyl. Since TID-10 detection does not involve the destructive Hydrogen-Air chemistry present in an NPD, its responses are much more dependent on the detailed electronegative character of the sample compound's molecular structure. Figure 3 compares the structures of Fentanyl, Heroin, and 6-Acetylmorphine to illustrate the correlation of TID-10 response and structure.

The main component of NPD and TID detectors is an ionizing surface comprised of ceramic material coated over a wire core, and the operating temperature of that surface is determined by the magnitude of electrical current flowing through the wire core. One of the unique characteristics of NPD and TID-10 detectors is that the absolute magnitude of sample response can be varied over a wide range by varying the surface temperature of the ion source. However, detector noise also varies with such surface temperature changes, so signal-to-noise should always be the best evaluator of performance for these type detectors rather than just absolute signal magnitudes. For the NPD data in Figure 2, the signal to noise ratio was 64000 for Fentanyl and 46000 for Heroin. For the TID-10 data, the signal to noise ratio for Heroin was 48000. Detector noise for these type detectors is related to the magnitude of detector background signal. For well designed NPD type of equipment, a general rule of thumb is that the noise is 0.001 times the background.

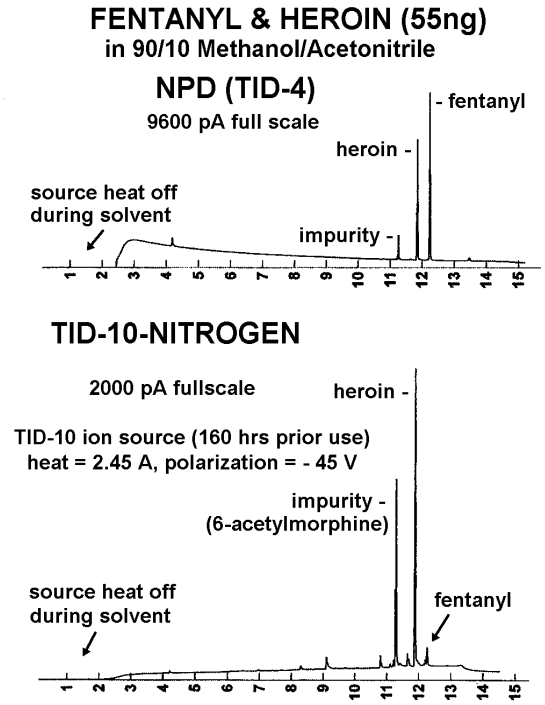
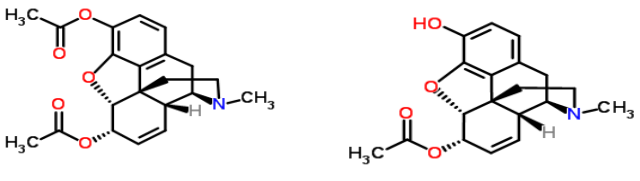
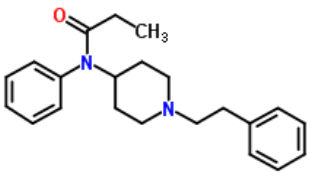


Figure 2. Same sample as Fig. 1. Detector gases for TID-10: N2 through "Air" line=60, N2 makeup=10 mL/min, N2 through "H2" line= setting of 2.

HEROIN **6-ACETYLMORPHINE**





FENTANYL

Figure 3.

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Figure 4 compares NPD and TID-10-Air chromatograms for a drug sample containing Methamphetamine (Speed), 3,4-MDMA (Ecstacy), Cocaine, and the Opiates, Morphine, Heroin, 6-Acetylmorphine, and Oxycodone.. As expected, the NPD provided responses for all these compounds. However, a TID-10 ion source operated in a detector gas environment of Air provided responses mainly to only the Opiate constituents of the sample. All of the Opiates in this sample had molecular structures similar to the Heroin and 6-Acetylmorphine structures shown in Figure 3, whereas the other drug constituents had significantly different structures as shown in Figure 5.

In Figure 4, the NPD produced signals of larger absolute magnitude,but background and noise were also about a factor of 3 higher, so TID-10 detectivity (signal-to-noise) was comparable to that of the NPD. In addition to its improved selectivity for just the Opiates, TID-10 detection is less complicated to implement because it does not require any Hydrogen, and can provide responses using just Nitrogen or Air as the detector gas.

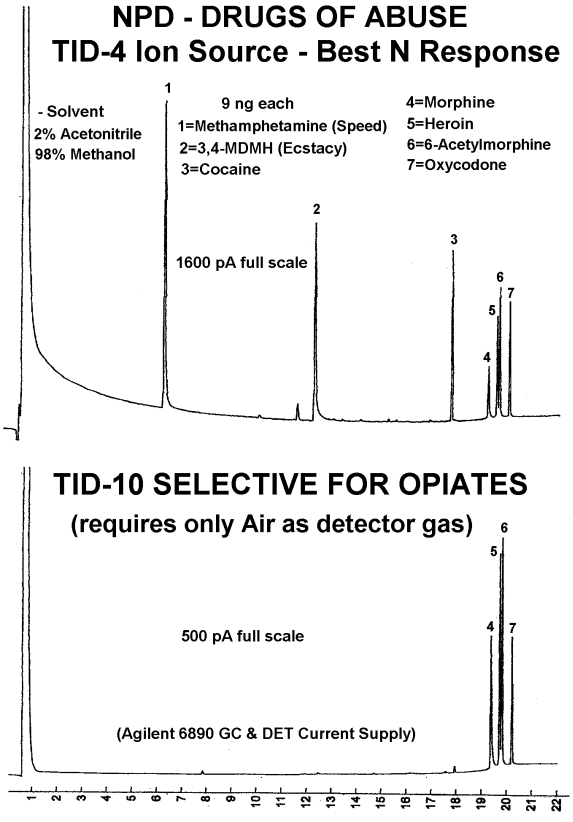
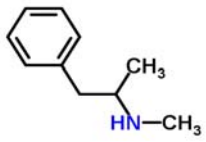
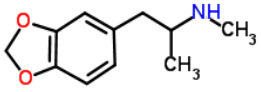


Figure 4. 30m x 0.53mm x 1.5µm DB-5ms, He=10mL/min 90-170°C at 7°C/min, 170-310°C at 16°C/min, 310°C-2min

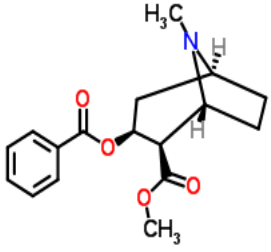
Figure 5.



METHAMPHETAMINE (SPEED)



3,4 MDMA (ECSTACY)



COCAINE

As with all of the data in this report, the detection equipment for Figure 4 included Agilent NPD hardware supplemented by a DET Current Supply to power the ion sources. As mentioned previously, TID-10 signal to noise gets bigger and bigger with increasing magnitude of the polarization voltage between the ion source and collector electrode. Figure 6 compares TID-10-Air responses using the DET Current Supply versus using Agilent's NPD Bead Voltage supply to power the ion source. The DET Current Supply data used an ion source polarization of - 45 V, whereas the Bead Voltage data was at Agilent's fixed polarization of - 4.4 V. The Opiate selectivity was the same at the different polarization voltages, but the higher polarization provided about 6 times larger signal magnitudes. The detector backgrounds for both chromatograms in Figure 6 were low enough that detector noise was the same 0.01 pA which was the inherent noise of Agilent's NPD electrometer used to measure ion current signals. Hence, the higher polarization provided about 6 times better detectivity. Some of this difference in detectivity can be recovered by operating the ion source at a higher surface temperature, but at the expense of a possible change in selectivity as well as a shorter operating life for the ion source.

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When using Agilent's Bead Voltage to power the ion source, the GC NPD status controls require some gas to be supplied through the "H_2" gas line in order to get a "Ready" state. For the data in Figure 6, this condition was satisfied by setting the H_2 flow at a minimal value of 0.5 mL/min. A better solution would have been to supply Nitrogen through the "Hydrogen" line.

Figure 7 shows NPD and TID-10-Air chromatograms for another mix of drug compounds including the 2 most widely encountered addictive drugs,Caffeine and Nicotine. For this sample, TID-10 ionization provided enhanced relative response for Diazepam versus Caffeine, a lower relative response for Cotinine versus Caffeine, and negligible response for Methamphetamine and Nicotine. Also included in Figure 7 is another illustration that a low ion source polarization that is typical of optimum NP detectors provides lower signal magnitudes, but retains the selectivity. Molecular structures for the Figure 7 sample are shown in Figure 8.

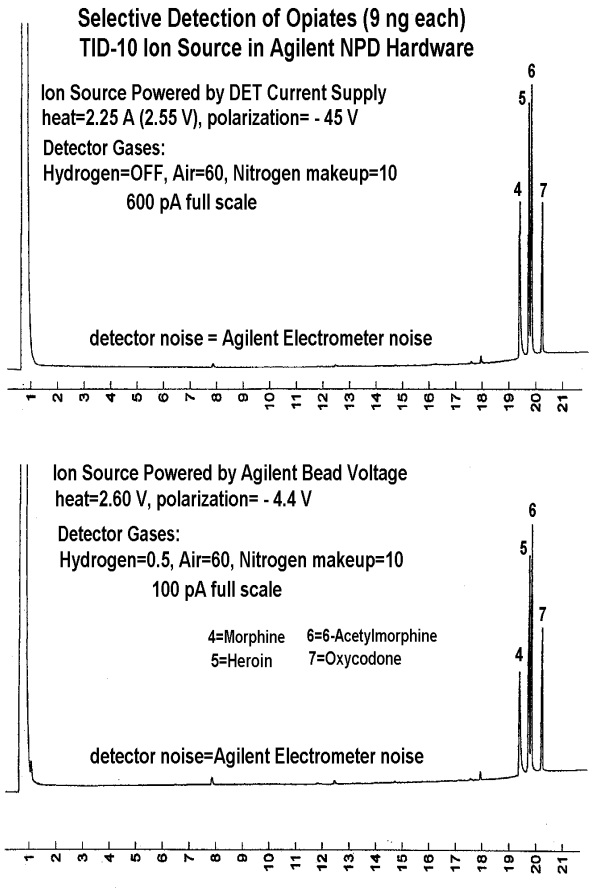

Figure 6. DET Current Supply polarization at - 45 V vs. Agilent Bead Voltage Supply at - 4.4 V polarization.

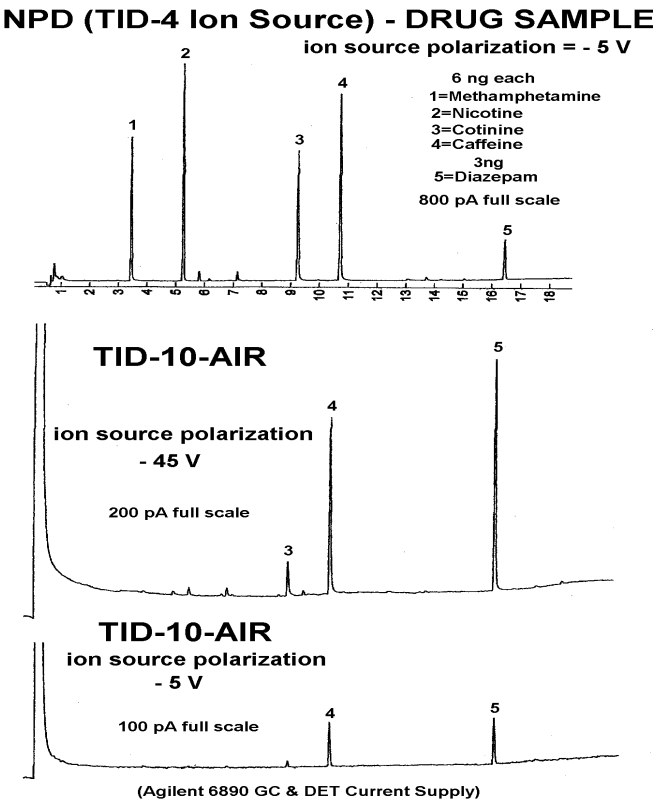

Figure 7. Same column as Figure 6. 110-300°C at 10°C/min, 300°C - 2 min.

NICOTINE **COTININE**

CAFFEINE **DIAZEPAM**

Figure 8. TID-10 responds to Cotinine, Caffeine, and Diazepam - all contain an Oxygen atom.

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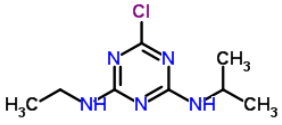
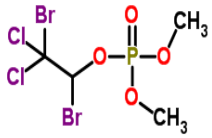
2.) MULTIPLE MODES OF SELECTIVE DETECTION FOR NALED, ATRAZINE, METHYL PARATHION, AND CHLORPYRIFOS.

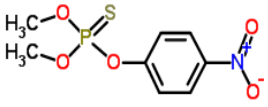
Naled is a mosquito control insecticide currently being used worldwide in the battle to control the spread of the Zika virus. Naled is an OrganoPhosphate compound which also contains electronegative Halogen atoms, so it is amenable to selective detection by an NPD, as well as by adaptions of NPD equipment to detection of electronegative compounds. Similarly, Methyl Parathion, Atrazine,and Chlorpyrifos are widely used agriculture pesticides which also can be detected by NPD and Halogen sensitive TID versions of NPD equipment. As mentioned previously, an adaption can often just involve an inexpensive substitution of a different type TID ion source for the NP ion source, plus a change in the composition of detector gases. To illustrate multi-mode adaptability of NPD equipment, a sample mixture was prepared using the 4 pesticides cited above, and whose molecular structures are shown in Figure 9. Analysis of this sample is shown in Figure 10 using NPD, TID-5, TID-3, and TID-10 modes of detection. TID-5 was similar to the NPD, but with enhanced relative responses to Atrazine and Chlorpyrifos. TID-3 detected just the Atrazine and Chlorpyrifos, while TID-10 detected just the Atrazine and Methyl Parathion. NPD and TID-5 required an ignited H_2 and Air detector gas environment, while no Hydrogen was required for the TID-3 and TID-10 modes.

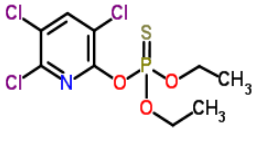
ATRAZINE **Figure 9** **NALED**





METHYL PARATHION **CHLORPYRIFOS**





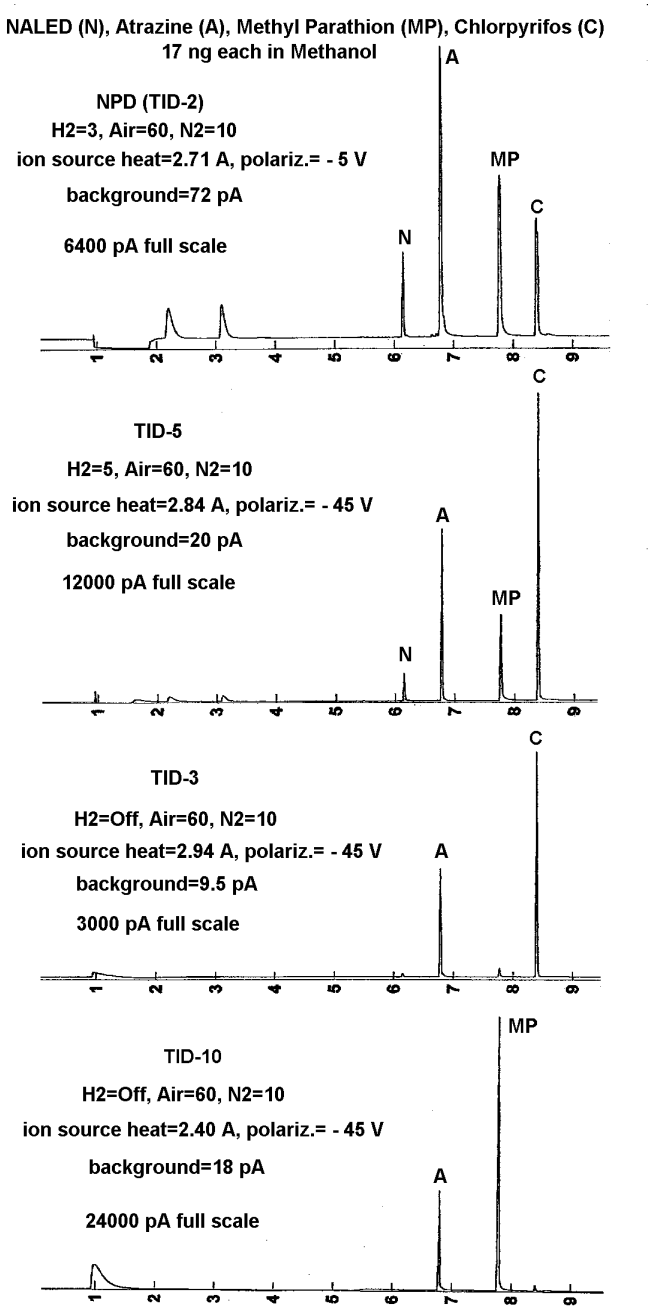


Figure 10. TID-2, TID-3, TID-5, and TID-10 are DET ceramic ion sources with different catalytic ionizing surface formulations for different compound selectivities.
Same column as Fig.1, He=3, 100-250°C at 15°C/min.

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3.) TID-10, NPD, TID-5, AND TID-3 DETECTION OF PYRETHROID INSECTICIDES.

Pyrethroids are a class of compounds widely used in commercial household insecticides. They all contain Oxygen atoms, so they are potentially amenable to selective detection by a TID-10 ion source. In addition, some Pyrethroids contain electronegative entities like Halogen atoms or the CN functional group, and are potentially detectable by NPD or other TID means.

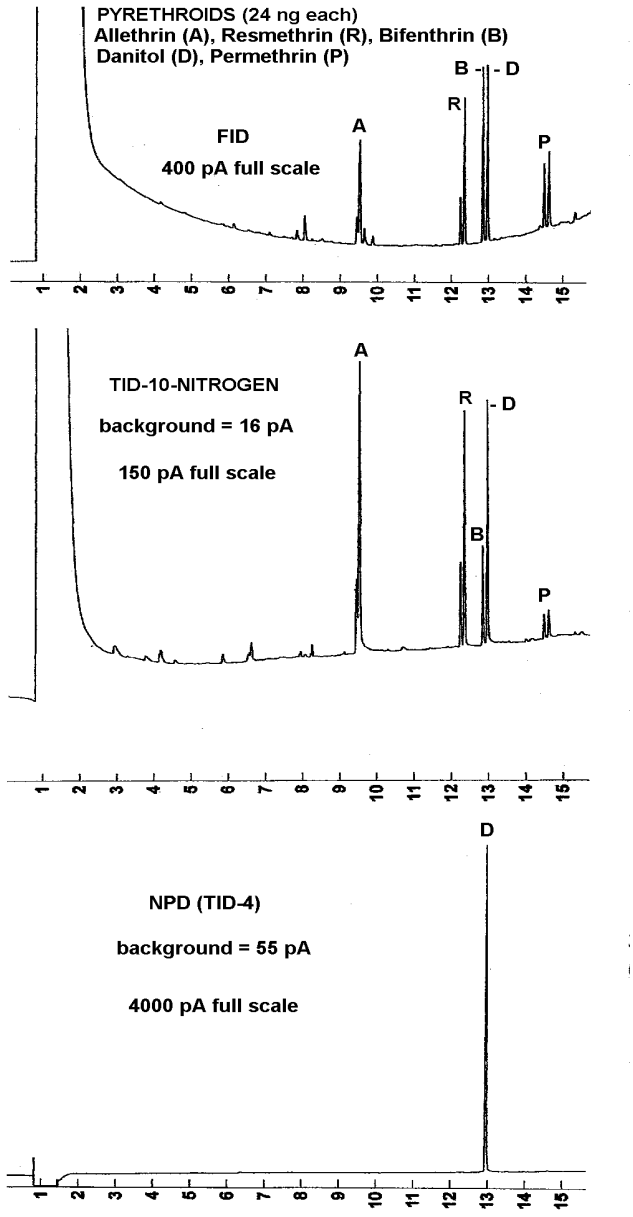

Figure 11. Same column as Figure 1. He=3mL/min 130-280°C at 10°C/min.

Figure 11 compares FID, TID-10, and NPD chromatograms of a mixture of Allethrin and Resmethrin which contain only O heteroatoms; Danitol (Fenpropathrin) which contains a CN functional group; Permethrin which contains Cl heteroatoms; and Bifenthrin which contains Cl and F heteroatoms. The standards used for these data included Allethrin, Resmethrin, and Permethrin isomers, so there were multiple peaks for each of these 3 compounds. As expected, TID-10 detection responded to the O atom content of all components of the mixture. Also as expected, the NPD provided a very large response to just the Danitol because of the CN group in that compound.

Figure 12 shows the same Pyrethroid sample analyzed with TID-5 and TID-3 modes of detection. Like the NPD, the TID-5 mode responded to the CN compound, Danitol, but also exhibited small responses to Bifenthrin and Permethrin which contained Halogen atoms. In the TID-3 mode of detection, the response to the Halogenated components became more evident relative to the CN compound.

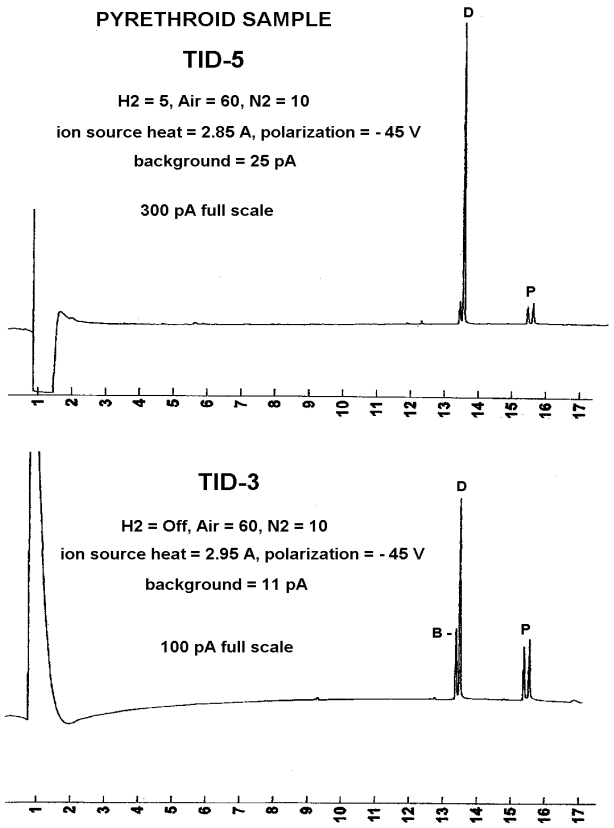

Figure 12.