

DET REPORT

NO.74 JANUARY 2017

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1.) CANNABIS COMPOUNDS (THC, CBD, CBN) - GC ANALYSIS WITH OXYGENATE SELECTIVE TID-10-AIR DETECTION.

2.) SULFUR RESPONSE OF SELECTIVE TID-10 SURFACE IONIZATION.

1.) CANNABIS COMPOUNDS (THC, CBD, CBN) - GC ANALYSIS WITH OXYGENATE SELECTIVE TID-AIR DETECTION.

Cannabis (Marijuana) remains the most widely used illegal drug in the world. However, the trend in more and more states in the USA is toward legalization. This has created a recent big interest in Cannabis chemical analyses amongst GC manufacturers and GC users. Because there are so many different types of Cannabis plants, there is a need to determine their psychoactive potency with regard to whether the Cannabis is to be used for recreational or medicinal purposes. The specific compounds of interest are Tetrahydrocannabinol (THC), Cannabidiol (CBD), and Cannabinol (CBN), with the molecular structures shown in Figure 1.

For growers and dispensers of Cannabis, the analysis requirement is the determination of THC, CBD, and CBN at relatively high sample concentrations with the least complicated and least expensive equipment. For forensics laboratories, the analysis requirements are detection of trace levels of Cannabis compounds in bodily fluids and/or hair. For environmental hazard laboratories, the analysis requirements are trace level detection of toxic pesticides that may have been used in growing the Cannabis plants.

GC analyses of Cannabis have mainly used FID or MS detection. However, since the all compounds shown in

Figure 1 contain "O" atoms, they are potentially detectable by DET's exclusive TID-10 Oxygenate selective mode of detection. This report describes newly identified TID-10 responses to THC, CBD, and CBN.

In comparison to an FID, TID-10 detection is a simplification in that it does not require any Hydrogen gas to support a flame. In comparison to MS, TID-10 detection requires much less complicated and less expensive equipment. Furthermore, in contrast to both FID and MS, TID-10 ionization detection provides a unique selectivity that can discriminate versus Hydrocarbons, as well as between different classes of Oxygenates. As a further advantage, TID-10 detection equipment is easily and inexpensively converted to selective detection of NP or Halogenated compounds for detecting pesticides used in cultivating the Cannabis plants.

Figure 2 compares FID and TID-10-Air chromatograms of a Cannabinoids mixture (Restek #34014) of CBD, THC (delta-9 isomer), and CBN. Both FID and TID data are displayed at the same full scale sensitivity, and it can be seen that both provided responses of similar absolute magnitude to the 3 Cannabinoids.

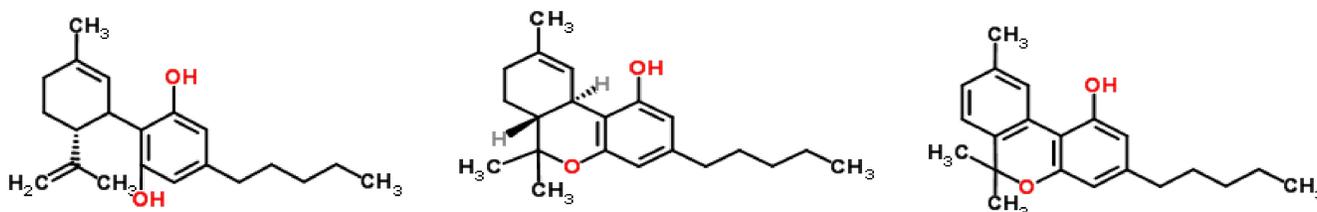


Figure 1. CBD

THC

CBN

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One difference between the detectors in Figure 2 was the detector gases required. Instead of the high flows of Hydrogen and Air needed for the FID, a small flow of Air sufficed for TID-10 detection. Not requiring Hydrogen is a big simplification in detection equipment for Cannabis compounds. The lower TID Air flow also represents a cost savings since it is not depleted as fast, and it does not have to be an ultra high purity grade as is normally used with an FID.

The other big difference between the Figure 2 chromatograms is the greatly suppressed Methanol solvent peak in the TID data. As discussed in previous

DET Reports, a TID-10 ion source responds to many types of Oxygenated compounds when operated in a inert gas environment of Nitrogen. However, when Air replaces the Nitrogen, responses from some classes of Oxygenates are suppressed compared to other Oxygenate classes. That is what was demonstrated in Figure 2 for the Alcohol solvent relative to the Cannabinoids. TID-10 detection also provides excellent selectivity versus many Hydrocarbon compounds.

Figure 3 compares FID and TID-10-Air chromatograms for a more diluted sample of CBD, THC, and CBN. Signal magnitudes were similar, and noise for both modes was such that detectivity could be projected to be in the low picogram range. The Methanol solvent suppression of the TID-10 mode provided less of a solvent peak disruption and a more stable baseline for later eluting Cannabinoid peaks.

The TID data in Figures 2 and 3 were obtained using a TID-10 ceramic ion source installed in Agilent 6890 NPD hardware designed to accommodate DET's standard ion source mounting. (NPD hardware on the Thermo Trace 1300 GC is similarly designed to accommodate the same ion source configuration.) Nitrogen was plumbed

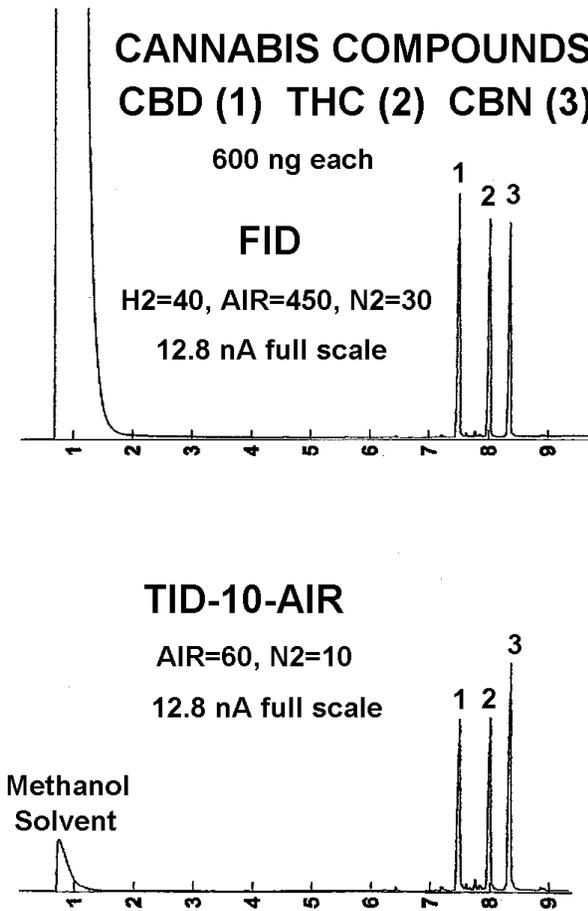


Figure 2. 0.6µL injected. 30m x .32mm x .25µm DB5ms, He=4mL/min, 150-290°C at 15°C/min. Agilent 6890 GC. TID-10 powered by DET Current Supply, heat=2.40A, polarization= - 45V.

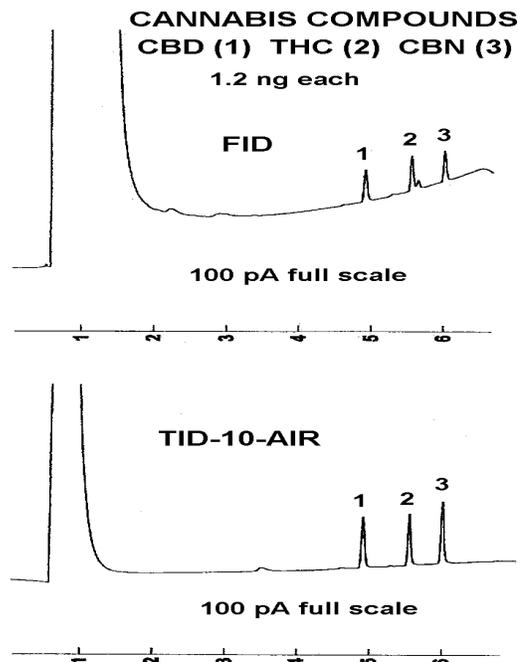


Figure 3. Same column as Figure 2. He=5mL/min, 200-265°C at 10°C/min.

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into the detector gas lines that normally provided NPD Hydrogen and Makeup, and Air was provided through the NPD Air line. The TID-10 ion source for these 2 figures was powered by a stand-alone DET Current Supply rather than using the resident Agilent NPD Bead Voltage supply. The reason for that was to achieve a higher polarization voltage between ion source and ion collector. TID-10 detection has the characteristic that signal to noise gets bigger and bigger with increasing polarization, in contrast to NP detection which is optimum at a low polarization. Agilent's Bead Voltage supply provides a fixed polarization of - 4.4 V, whereas the DET supply provides - 5, - 15, and - 45 V selection for optimum performance in both NPD and TID detection modes. (Thermo is currently the only GC manufacturer with NPD electronics that allows setting ion source polarization anywhere in the range of - 3 V to - 100 V.)

The top two chromatograms in Figure 4 illustrate the difference between high and low polarizations for TID-10 ionization signals. The - 5 V chromatogram represented selective detection signals that would be obtained if the resident Agilent Bead Voltage was used to power the

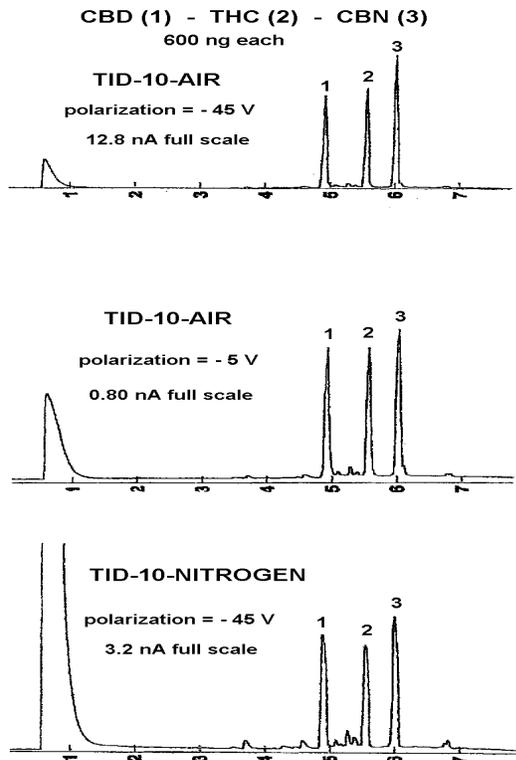


Figure 4. Same conditions as Figure 3.

ion source. As can be seen, Cannabinoid responses were about 16 times smaller with the lower polarization. The bottom chromatogram in Figure 4 shows the difference with Nitrogen rather than Air as detector gas..

The TID-10 data described in this report involved adaption of equipment originally designed for NP detection. That adaption is easily reversed back to NPD or other modes through simple changes in the ion source and composition of detector gases. Hence, in addition to detection of Cannabinoid compounds, the same basic equipment can be used to examine Cannabis samples for the presence of trace level pesticides. Figure 5 illustrates multiple detection modes for a sample of commonly used pesticides.

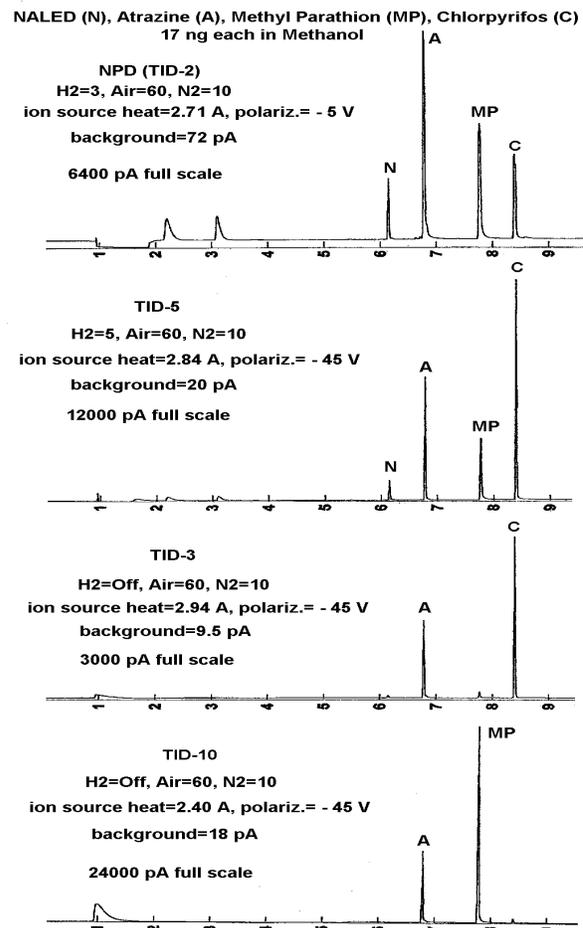


Figure 5. TID-2, TID-3, TID-5, and TID-10 are DET ceramic ion sources with different catalytic ionizing surface formulations for different compound selectivities. Same column as Fig. 2, He=3, 100-250°C at 15°C/min.

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The TID-10-Air chromatogram at the bottom of Figure 5 was the same mode of detection as used for the Cannabis data in Figures 2 - 4. The exceptional sensitivity for the Atrazine component of the Fig. 5 sample was due to the presence of a highly electronegative Cl atom located in a para position relative to other functionalities in that compound's molecular structure. Similarly, the exceptional sensitivity to Methyl Parathion was due to the presence of an electronegative NO₂ group in a para location in that molecule. In a TID-10-Air analysis of a Cannabis plant, these and similar trace pesticides would contribute chromatographic peaks in addition to the CBD, THC, and CBN peaks. Hence, Cannabis potency and possible pesticide contamination could be revealed in the same analysis.

As already mentioned, data in this report were generated with an Agilent 6890 GC equipped with NPD detector hardware and electronics. Conversion to Cannabis detection was accomplished by substitution of a TID-10 ion source (\$495 USD) into the hardware, and substitution of a DET Current Supply (\$2244 USD) to get the largest possible TID-10 signals. A similar substitution of just the TID-10 ion source in Thermo Trace 1300 NPD equipment would also suffice for these analyses. For some other older GC NPD models, DET has available

retrofit hardware that can be easily mounted onto the GC in order to accommodate DET ion sources. This retrofit equipment is as follows:

Thermo Trace Ultra NPD/GC: DET Retrofit NPD/TID/CCID tower structure (\$2340 USD) fits Thermo detector base, and accommodates any DET ion source; Thermo NPD electronics provide optimum power for all modes.

Varian TSD/GC Models: DET NPD/TID/CCID tower (\$2100 USD) fits Varian detector base; ion sources can be powered by Varian TSD electronics, but best TID-10 sensitivity is achieved with the higher polarization available from a DET Current Supply;

SRI Instruments FID/NPD GC Models; DET retrofit NPD/TID/CCID tower (\$2340) fits SRI detector base and provides same detector and ion source configuration as used on Agilent/Thermo NPDs; ion sources can be powered with SRI's NPD or FID electronics, or with a DET Current Supply for finer control/higher polarization.

For older GC models that still have functioning Injector, Column oven, and Detector Thermal Zones and Pneumatics, a detector retrofit is a cost effective means of extending the useful life of the GC, and at the same time adding selective detection capability not previously available on that GC.

2.) SULFUR RESPONSE OF SELECTIVE TID-10 SURFACE IONIZATION.

O, N, S, and P are the four most common occurring heteroatoms in organic chemistry. Previous DET Reports have described how detector equipment designed for selective detection of N or P compounds can be converted to selective detection of O compounds. Oxygenate selectivity is achieved using a catalytically active ceramic TID-10 ion source operated in either a Nitrogen or Air detector gas environment. This current report describes TID-10 surface ionization detection of S compounds.

There are, of course, other widely used Sulfur Selective detectors such as the Sulfur Chemiluminescence Detector (SCD), Flame Photometric Detector (FPD), and Pulsed Flame Photometric Detector (PFPD). These 3 detectors all involve sample decomposition, and sensing of selective light emissions involving the decomposition products. The emitted light is converted to detectable electrical signals by photometric means external to the detection volume. As a result of the sample decomposition, these 3 detectors tend to provide S

responses independent of how the S atom was bound up in the sample molecule.

By contrast, TID-10 Surface Ionization does not involve sample decomposition. Instead, sample compounds are converted directly into electrical signals upon impact with the electrically heated TID-10 surface within the internal volume of the detector structure. Consequently, it is more likely that any TID-10 responses to S compounds will depend on the sample compound's molecular structure. This report examines TID-10 ionization for several different classes of S compounds.

Figure 6 compares FID and TID-10-Nitrogen chromatograms for a sample containing the S compound, tert-Butyl Disulfide, plus Hydrocarbons and other Heteroatom compounds. As can be seen, TID-10 ionization provided exceptionally good selectivity and sensitivity for this S compound that has the molecular structure shown in Figure 7. The TID-10 chromatogram

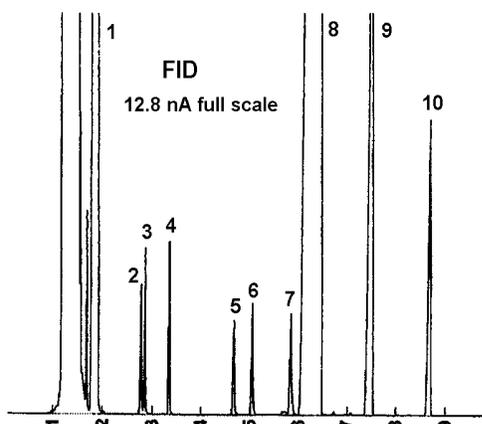
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demonstrated the degree of selectivity versus Linear Chain Alkanes, as well as the iso-Octane solvent. In addition, selectivity was exhibited versus various other constituents containing Br, Cl, F, N, and Si heteroatoms.

HYDROCARBON & HETEROATOM COMPOUND MIX



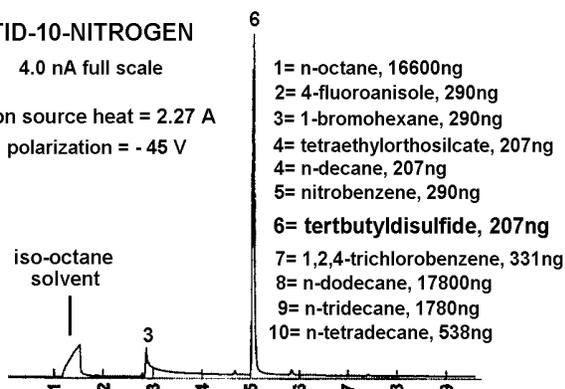
TID-10-NITROGEN

4.0 nA full scale

ion source heat = 2.27 A

polarization = - 45 V

iso-octane solvent



- 1= n-octane, 16600ng
- 2= 4-fluoroanisole, 290ng
- 3= 1-bromohexane, 290ng
- 4= tetraethylorthosilicate, 207ng
- 4= n-decane, 207ng
- 5= nitrobenzene, 290ng
- 6= tertbutyldisulfide, 207ng
- 7= 1,2,4-trichlorobenzene, 331ng
- 8= n-dodecane, 17800ng
- 9= n-tridecane, 1780ng
- 10= n-tetradecane, 538ng

Figure 6. Same column as Figure 2. He=4. 60-210°C at 10°C/min. (This sample mix was originally used to test the Atomic Emission Detector (AED) sold many years ago by Agilent.)

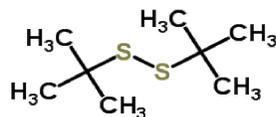
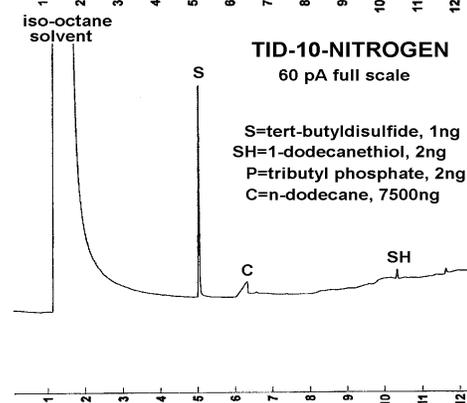
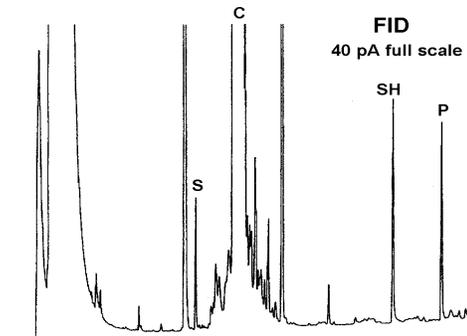


Figure 7. Molecular structure of tert-Butyl Disulfide. Large TID-10 response.

Selective TID-10 detection of tert-Butyl Disulfide is also demonstrated by comparison with FID data shown in Figure 8. The sample for this figure was Agilent's FPD Test Sample. The FID chromatogram revealed the presence many Hydrocarbon impurities in the sample which were not detected in the TID-10 chromatogram. In addition to tert-Butyl Disulfide, another S compound in the sample was 1-Dodecanethiol which had a TID-10 pA/ng response factor about 50 times less than that of tert-Butyl Disulfide. Nevertheless, Thiol compounds, in general, can be selectively detected at nanogram and higher levels by the TID-10 surface ionization process as shown in Figure 9. Whereas a compound like tert-Butyl Disulfide is detectable at low picogram levels, detectivity for Thiols is in the 0.1ng to 1ng range.

AGILENT FPD TEST SAMPLE



- S=tert-butyldisulfide, 1ng
- SH=1-dodecanethiol, 2ng
- P=tributyl phosphate, 2ng
- C=n-dodecane, 7500ng

Figure 8. Same column as Fig.2. He=4. 60-260°C at 10°C/min.

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Figure 9 compares FID and TID-10 chromatograms for the situations where the TID-10 ion source was operated in Air and in Nitrogen detector gas environments. Using the same ion source heating current and polarization, a change from Nitrogen to Air as the detector gas resulted in some suppression of the magnitude of TID-10 responses to Thiols. This is a characteristic analogous to previous reports regarding Alcohols. Also, a detector gas environment containing Oxygen can be expected to contribute additional TID-10 response for high concentration Linear Chain Thiols as generated by the onset of the process of Catalytic Combustion Ionization associated with the numbers of CH₂ groups present in the sample molecule.

A feature of the TID-10-Nitrogen data in Figure 9 is the large response for 3,5-Dimethyl Benzenethiol compared to the other Thiols. This is similar to previously reported differences between Phenols and Alcohols. Figure 10 shows comparative molecular structures.

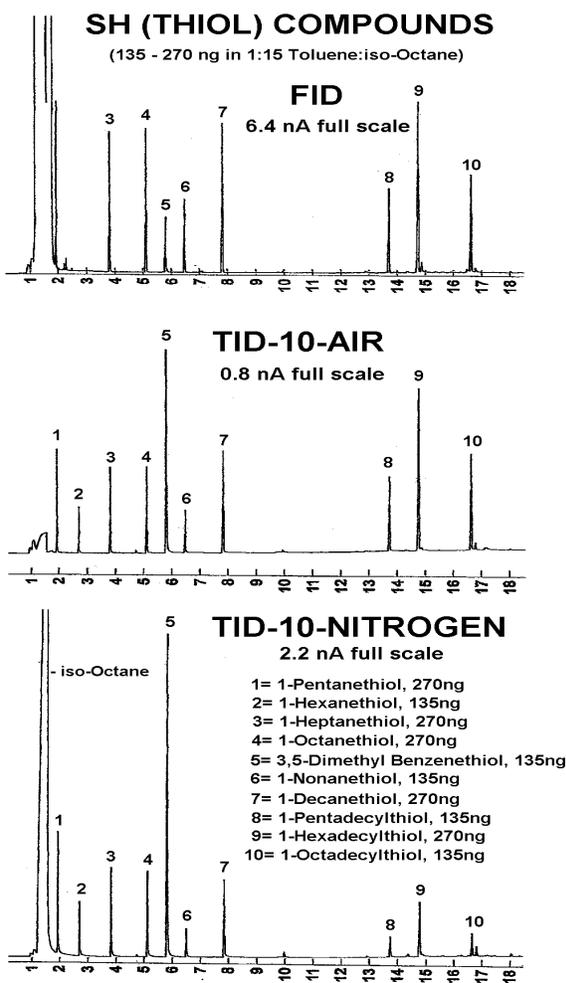


Figure 9. Same column and program as Figure 8.



3,5-Dimethyl Benzenethiol

1-Pentanethiol

Another S compound that has an exceptionally good TID-10-Nitrogen response is Allyl Isothiocyanate with the molecular structure shown in Figure 11.

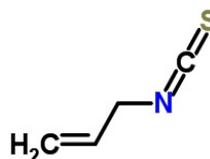


Figure 11.
Molecular structure of
Allyl Isothiocyanate.
Large TID-10 response.

Equally important is identification of S compounds that have negligible TID-10 response. Molecular structures of 2 of those are shown in Figure 12.



Fig. 12. Thiophene

Dimethyl Sulfide

Negligible TID-10 response.

In summary, TID-10 ionization provides selective detection for various S compounds, with responses depending on the molecular structure class of the compound. Compounds containing the SH functional group as well as Disulfides are especially responsive. The same detector also responds to many Oxygenated compounds, so a TID-10 chromatogram could contain both "S" and "O" compound peaks, while discriminating versus Hydrocarbons. In a comparison, TID-10-Nitrogen was found to have about a factor of 2 larger response to 1-decanethiol than to 1-decanol.