

DET REPORT

NO.72 OCTOBER 2016

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- 1.) CONVERTING NPD EQUIPMENT TO TID-10 OXYGENATE SELECTIVITY.
- 2.) SELECTIVE RESPONSES FOR DIFFERENT CLASSES OF OXYGENATES.
 - a.) Alcohols; b.) Acids; c.) Glycols & Phenols; d.) Flavors & Fragrances;
 - e.) FAMES & Triglycerides.
- 3.) RESIDUAL CAFFEINE AND VANILLA FLAVORING IN "DECAFFEINATED" AND "CAFFEINE FREE" TEAS (INTERCHANGEABLE NPD AND TID-10).

1.) CONVERTING NPD EQUIPMENT TO TID-10 OXYGENATE SELECTIVITY

Figure 1 depicts NPD equipment used on Agilent 6890/7890 and Thermo Trace 1300 GCs, as well as on all DET detector retrofits for other GC models. Key features are an electrically heated ion source (bead) positioned on the axis of an ion collector, and a detector gas environment consisting of a dilute mix of Hydrogen in Air. In contrast to glass bead NP ion sources like the so-called "Blos Bead", DET has pioneered ion sources made of ceramic materials, and this technology has allowed development of different ceramic formulations that provide ionizing selectivity other than just NP. **The most significant of these other modes is selectivity for Oxygenated compounds because "O" is the most commonly occurring heteroatom in organic chemistry.**

Figure 2 depicts how NPD equipment is transformed for Oxygenate selective detection. A TID-10 ceramic ion source replaces TID-2 or TID-4 ceramics that are used for NP detection, and the detector gas environment is only Nitrogen or Air (i.e., no Hydrogen required.) **This conversion from "NP" to "O" selectivity is simple, inexpensive, and interchangeable, and it greatly expands the number of possible applications for the same basic equipment.**

NPD (Nitrogen/Phosphorus Selective)

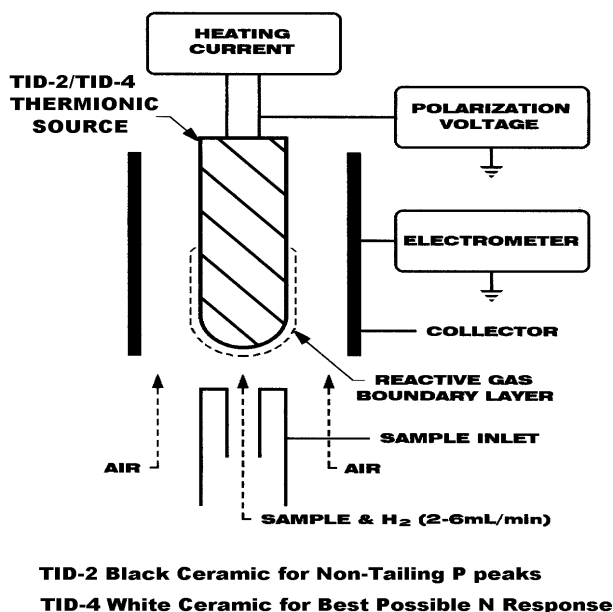


Figure 1. NP selective detection

TID-10 Themionic Surface Ionization (Oxygenates & some other Electronegatives)

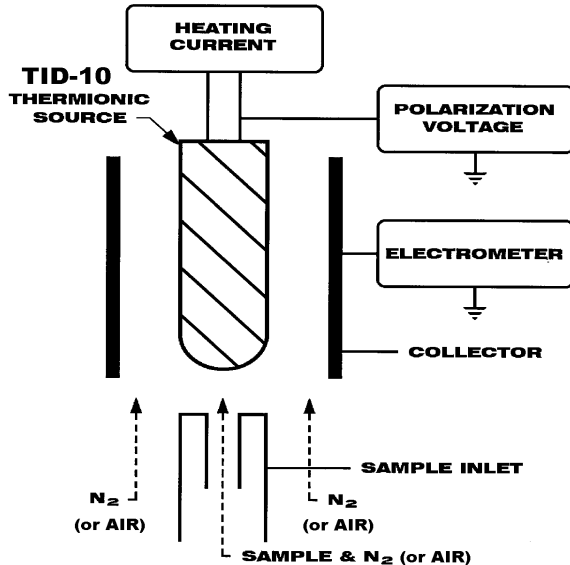


Figure 2. "O" selective detection

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The hardware components illustrated in Figures 1 and 2 are contained in a tower structure mounted onto a detector base with lines for supplying 3 different detector gases. For NPD, those gases are Hydrogen, Air, and Makeup (usually Nitrogen). For "O" selectivity, the required gas environment is either Nitrogen, Air, or a combination thereof, supplied through the 3 detector gas lines.

NPD hardware on Agilent, Thermo, and DET Retrofits are configured for ion source access from the top of the tower, so that ion source changes are easy and require minimal instrument downtime. NPD towers on Agilent 6890/7890 and Thermo Trace 1300 GC models were designed to accommodate DET's standard ion source mounting. DET Retrofit hardware allows the same ion source compatibility to be achieved on Varian/Bruker/Scion, Thermo Trace Ultra, HP 5890, and SRI Instruments GC models.

DET ion sources consist of a wire core covered by several layers of ceramic coatings, with the outer most surface coating defining the selectivity of ionization. A TID-10 ion source is a more robust version of an earlier TID-1 source, and it is a catalytically active ceramic characterized by a low work function for the emission of electrical charge. The basic operating mechanism of TID-10 oxygenate detection is a surface ionization process where the sample compound impacts the surface, extracts a negative charge, and the resultant negative ions move through the detector gas to be measured at the collector electrode.

NPD electronics on Agilent, Thermo, Varian/Bruker/Scion, and SRI Instruments include means of supplying electrical heating current to the ion source wire core, as well as polarizing the ion source at a negative voltage relative to the collector. Existing NPD Electrometers on those instruments suffice for signal measurement from TID-10 as well as NPD modes.

The magnitude of ion source polarization voltage is one area where there is a differing consideration between NPD and TID-10 modes. For NPDs, the polarization is usually a low value of - 4 or - 5 V in order to achieve best signal to noise and best selectivity of NP versus C. In contrast, best TID-10 selectivity and signal to noise is achieved by polarizations of - 45 V or higher. Among GC manufacturers, only Thermo provides NPD electronics in which polarization can be adjusted from - 3 V to - 100 V. On other GC models, existing NPD electronics are fixed at the low value optimum for NPD, and TID-10 responses are not as good as they could be with a higher polarization. For those GC models, DET has available a substitute stand-alone Current Supply module that can be used to heat ion sources, and polarize them at switch selectable values of - 5 V, - 15 V, or - 45 V for optimum performance in all modes of detection. Most of the data

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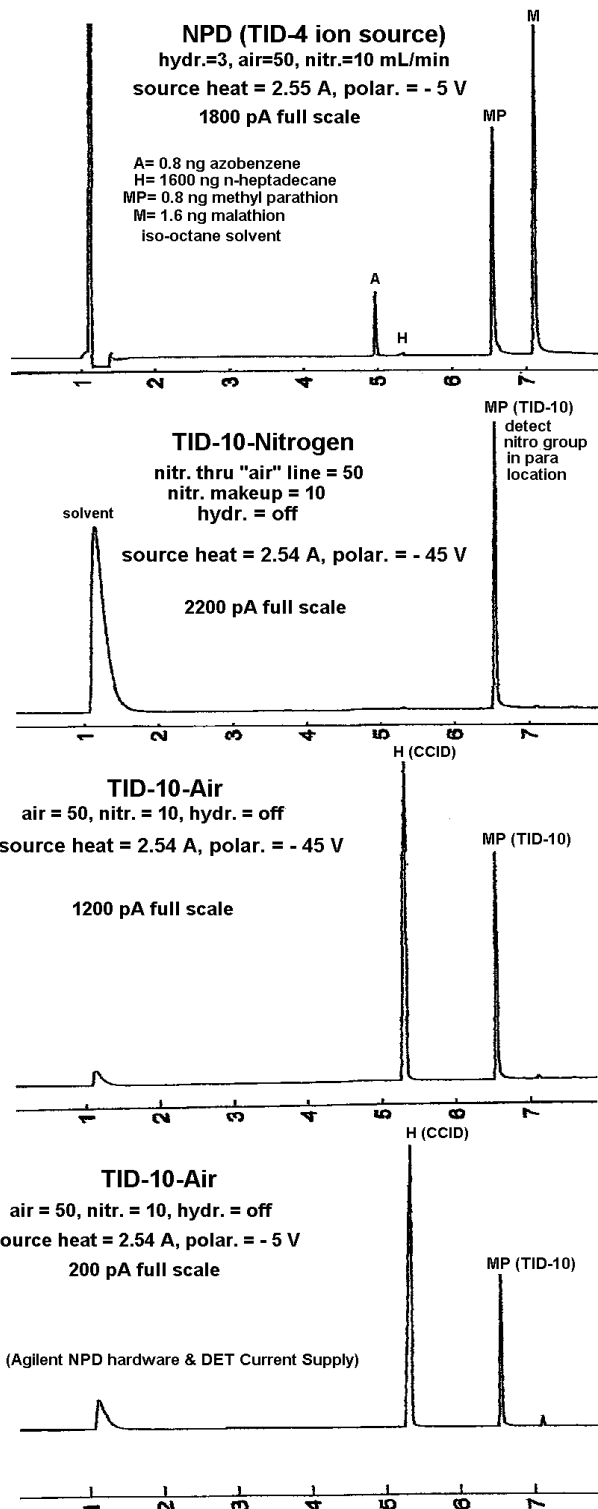


Figure 3.

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presented in this report were obtained using this DET Current Supply. The bottom 2 chromatograms in Figure 3 show the difference between TID-10-Air response at - 5 V versus - 45 V polarization.

The sample analyzed in Figure 3 was the NPD test sample used to demonstrate performance of the NPD (TSD) detector on Varian/Bruker/Scion GC models. It contained trace amounts of Azobenzene (N compound), Methyl Parathion (N,P compound), and Malathion (P compound), as well as a much larger concentration of Heptadecane as a representative C compound. As shown in Figure 3, the same test sample also works very well to illustrate TID-10 and NPD differences.

Although TID-10 responds to most compounds containing "O" atoms, the response differs depending on the type of Oxygenated compound. One class of compounds with especially large responses are those containing the Nitro (NO₂) functional group, and, in particular, the Nitro group located in a para position relative to other functionalities in the compound's molecular structure. That was the case for the Methyl Parathion component of Figure 3, and is the case for similar compounds like 4-Nitrophenol or TNT.

As a general rule, TID-10 provides the best selectivity for Oxygenated compounds when the detector gas environment is inert Nitrogen. When the gas environment

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is changed to Air, the response to some classes of Oxygenates are diminished while others remain unchanged or enhanced. Also, with the presence of O₂ in the detector gases, a TID-10 ion source can contribute to a different detection process of Catalytic Combustion Ionization (CCID) that provides responses to high concentrations of compounds containing chains of Methylene (CH₂) functional groups. Accordingly, the data in Figure 3 corresponding to Air in the detector gas illustrate CCID response to the Heptadecane component of the sample, as well as TID-10 Surface Ionization response to the Methyl Parathion component of the sample.

For the NPD and TID-10 data in Figure 3, the detector background signal magnitude was in the range of 10 - 15 pA. That meant that the detector noise for all data was essentially just the 0.02 pA noise of the Agilent Electrometer. Therefore, signal to noise ratios for the NPD and TID-10 (- 45 V) were sufficiently large to correspond to sub-picogram detectivities for the Azobenzene, Methyl Parathion, and Malathion components of the sample. In contrast, the CCID response to the Heptadecane component was due to that compound fueling a momentary burst of flame ionization as it impacted the TID-10 surface. That process is characterized by a response threshold in compound amount which is about 200 ng for Heptadecane.

2.) SELECTIVE RESPONSES FOR DIFFERENT CLASSES OF OXYGENATES.

a.) Alcohols

Figure 4 is a signature chromatogram comparison illustrating the simplification provided by a TID-10 ion source for the selective detection of an Oxygenated compound in a complex Hydrocarbon matrix. For the Gasoline sample analyzed, there wasn't a need to chromatographically resolve all the sample constituents because Ethanol was the only constituent detected with any significant magnitude.

As will be seen, Alcohols are not the highest responding class of Oxygenates for TID-10 detection. However, they are a convenient point of reference when examining other classes.

Figure 5 shows a comparison of chromatograms for a prepared mixture consisting of 5.5% each of 12 Alcohols plus the Hydrocarbon n-Tetradecane. The mix also contained 28.5% of n-Hexane. As expected, an FID provided large responses to all the compounds in the sample, while TID-10-Nitrogen responded only to the Alcohols. As a general rule, TID-10-Nitrogen sensitivity to Alcohols is not as large as an FID as Figure 5 shows.

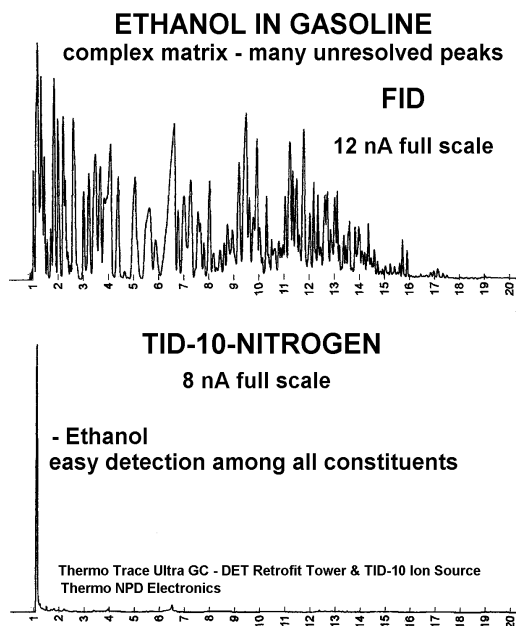


Figure 4.

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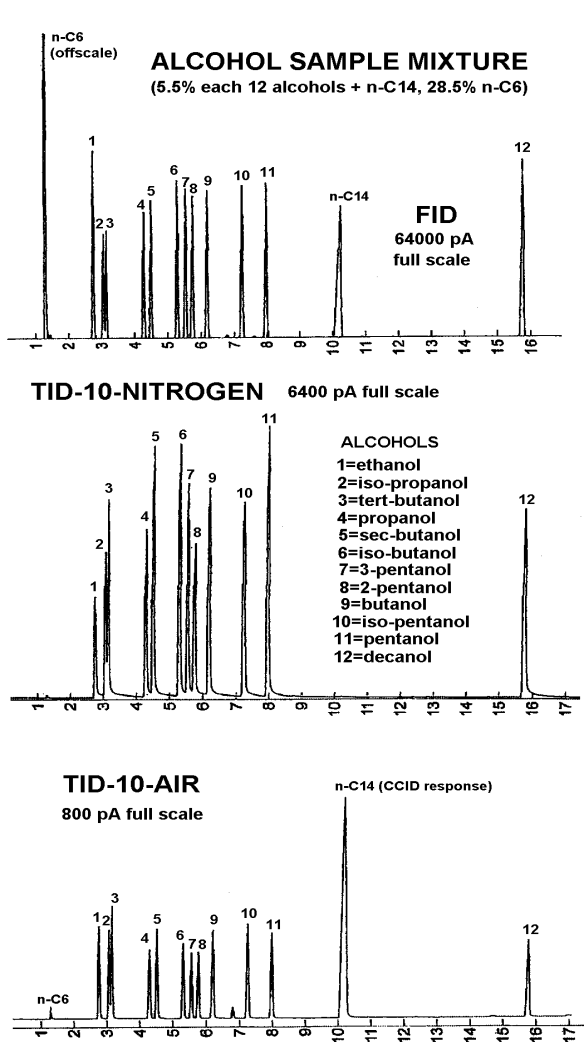


Figure 5. Agilent 6890 GC. TID data obtained with Agilent NPD hardware, DET TID-10 ion source, & DET Current Supply at -45 V. N₂ (Air) thru "Air" line=50, N₂ makeup=10; H₂=Off, He carrier=6mL/min; 0.1 µL sample injected; 30m x .53mm x 1.0µ DB Waxetr, 40-170°C at 8°C/min

However TID-10-Nitrogen provides a selectivity not available with an FID, and this can allow better detection of Alcohols in complex real world sample cases such as Figure 4. Furthermore, TID-1-Nitrogen is much simpler to implement since it requires only Nitrogen as a detector gas, and that gas does not have to be an ultrahigh grade. By comparison, an FID requires high purity Hydrogen and Air, and its equipment must include a flame ignitor and a jet to support the flame.

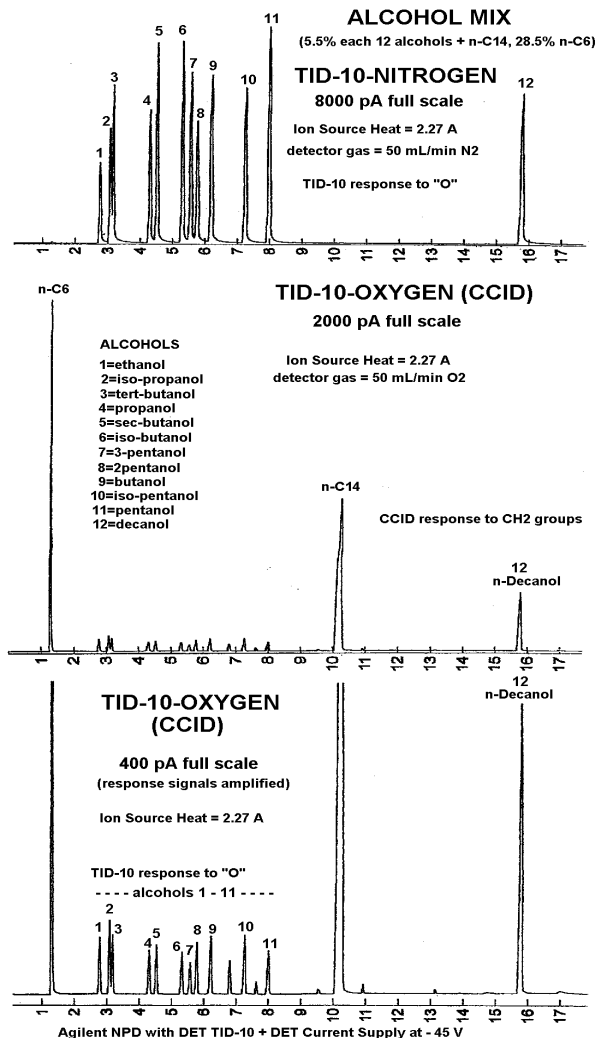


Figure 6. O₂ thru "Air" line=50, N₂ makeup=10.

The bottom chromatogram in Figure 5 illustrates changes that occurred when Air replaced Nitrogen as the detector gas. First of all, the Air resulted in a substantial reduction in the magnitude of TID-10 responses to the Alcohols. At the same time, the presence of Oxygen in the detector environment began to add in CCID responses to the CH₂ groups present in the Hydrocarbon constituents of the sample.

Figure 6 shows further changes that occurred when O₂ replaced Air in the detector gas environment. CCID responses to CH₂ groups in the Hydrocarbon and Decanol constituents now predominated.

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TID-10 selective detection provides different magnitudes of response for different classes of Oxygenates. Figure 7 illustrates FID and TID-10 chromatograms for a sample containing representative Alcohol, Acetate, and Ketone compounds. As shown, the Diketone compound, Diacetyl, had an especially large TID-10 response compared to the other Oxygenates. Furthermore, the TID-10 data revealed

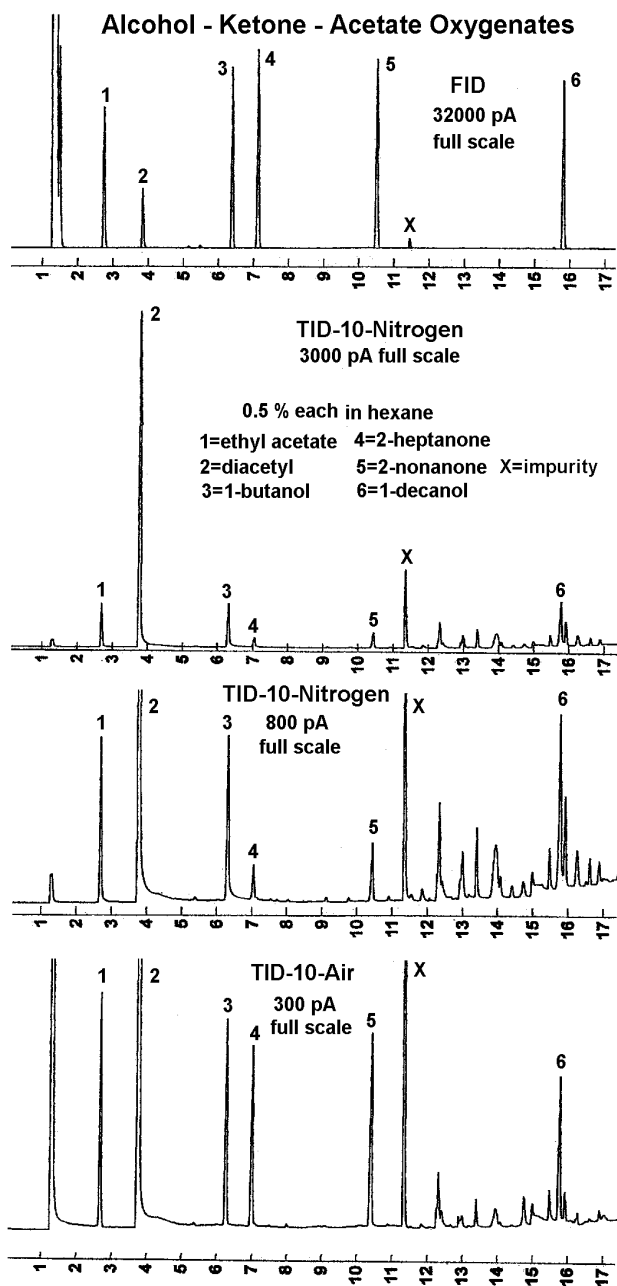


Figure 7. Agilent 6890, 30m x 0.53mm x 1.0µm DBWax He=6, 40-180°C at 8°C/min, TID-10 powered with DET Current Supply, 2.46 A, polarization - 45 V.

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that the analyzed sample contained many more impurity constituents not evident in the FID chromatogram. This is not unusual in our experience using TID-10 ion sources. Sample mixtures comprised of purchased standards are often found to have extra Heteroatom compounds which are not well detected by an FID.

Aside from the large Diacetyl response, the TID-10 data in Figure 7 show that Ketone responses were about a third the magnitude of Acetate and Alcohol responses when the detector gas environment was Nitrogen, and more comparable to the Acetate and Alcohol responses when the detector gas was Air.

An interesting characteristic of TID-10 detection is that it is non-destructive, so that compound aromas can be sensed as they elute from the detector exit port. For this sensing purpose, elution in a detector gas stream of Air versus Nitrogen provides more readily identified aromas. For the impurity labeled "X" in Figure 7, its aroma indicated it was Acetic Acid, and that was confirmed by comparison with the retention time of an Acetic Acid standard. Like Diacetyl, Volatile Acids are a class of Oxygenates exhibiting much larger TID-10 responses than Acetates, Alcohols, or Ketones.

Ethers are an Oxygenate class with a much lower TID-10 response than Alcohols. This is demonstrated in the data of Figure 8 for a sample mix of 5.2% MTBE and 0.65% Ethanol in Water. The MTBE standard used for these data contained a Methanol impurity evident in the TID-10 chromatogram, but not in the FID chromatogram.

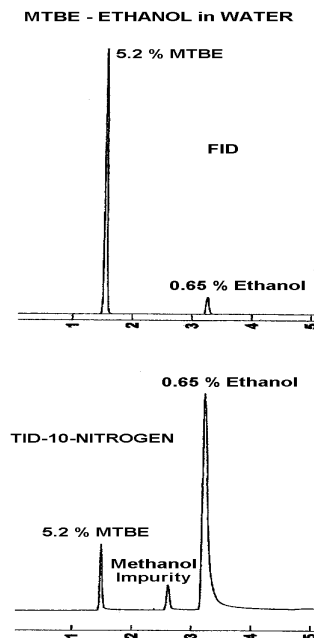


Figure 8.

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b.) Acids

Volatile Carboxylic Acids are a class of Oxygenates often encountered in analyses of real world food and beverage samples. TID-10 detection of acids includes response to Formic Acid which is not detected by an FID as shown in Figure 9. Consequently, reported FID analyses of samples such as Alcoholic Beverages do not mention Formic Acid, whereas TID-10 detection readily reveals the presence of this strong flavor and aroma compound as demonstrated in Figure 10.

TID-10 detection is especially well suited to analyses of Alcoholic Beverages because of the enhanced response for Acids versus Alcohols. Using Air in the detector gas environment provides further suppression of the Ethanol response, so that Acids are even more enhanced in the chromatogram. Figure 11 demonstrates this, as well as the fact that TID-10-Air and TID-10-Nitrogen can produce different chromatographic fingerprints for the same sample. If the analysis goal is to determine Lactic Acid and Glycerol in a wine, then TID-10-Nitrogen is the best choice. If the analysis goal is best detection of the Acids, then TID-10-Air provides better suppression of Alcohol and Glycerol responses. Operation of a TID-10 ion source in an oxidizing Air or O₂ detector gas can sometimes alter the response characteristics of that ion source when the detector gas environment is changed back to inert N₂. Consequently, it is best to dedicate a particular TID-10 ion source to operation in either the inert or oxidizing environment whenever possible.

CARBOXYLIC ACIDS & GLYCEROL Wine - Oxygenate Selective TID-10

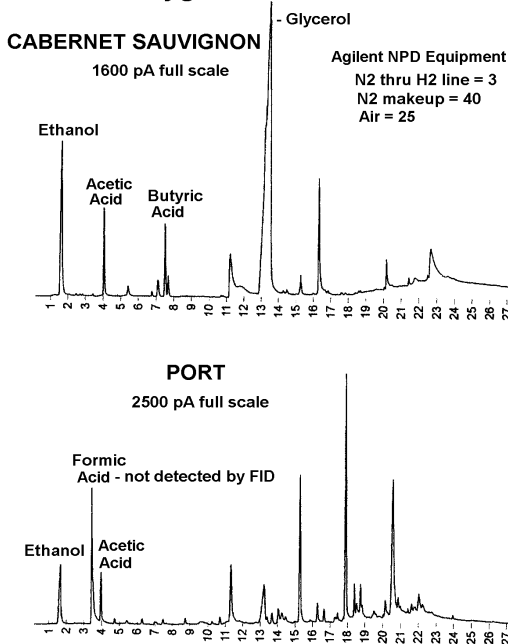


Figure 10

FORMIC (F) & ACETIC (A) ACIDS 0.1 % each in Water (W)

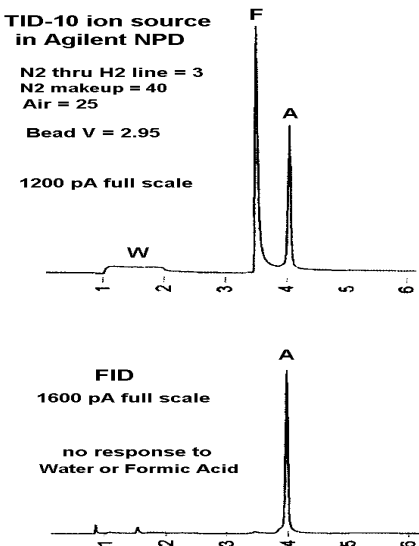


Figure 9.

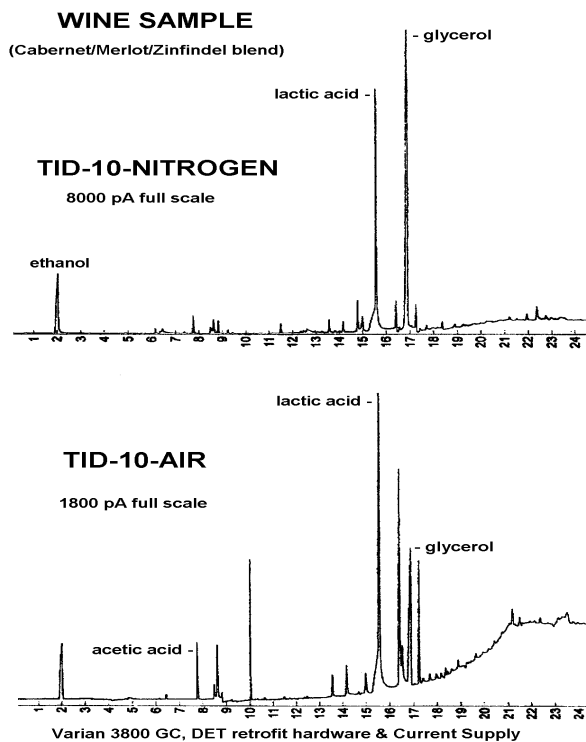


Figure 11.

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Volatile Carboxylic Acids are also compounds produced in oxidative degradation of food and petroleum products. Figure 12 illustrates TID-10-Air analyses of Methanol extracts of a Cheese sample before and after the appearance of Mold on the Cheese. Figure 13 illustrates sensitive and selective TID-10-Nitrogen detection of degradation products present in an aged Biofuel sample which had developed a rancid odor. Figure 14 illustrates selective TID-10-Nitrogen detection of oxidative degradation compounds that built up with miles of usage of a motor oil.

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AGED B100 BIODIESEL (4% in n-Heptane)

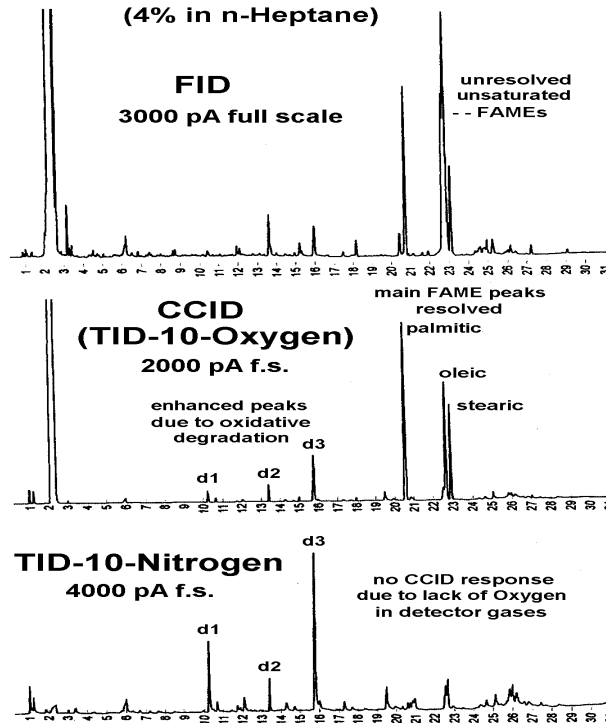


Figure 13. Selectivity of CCID detection resolved the main FAME constituents in the sample compared to the unresolved FID peaks. TID-10-Nitrogen more clearly revealed products of oxidative degradation of the Biofuel.

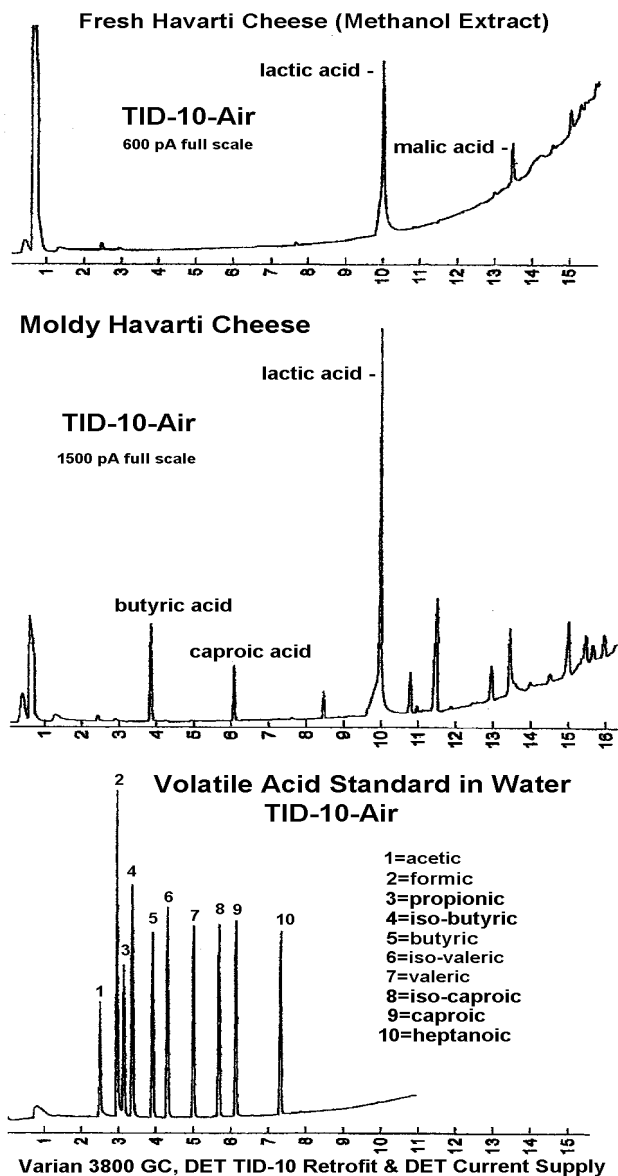


Figure 12

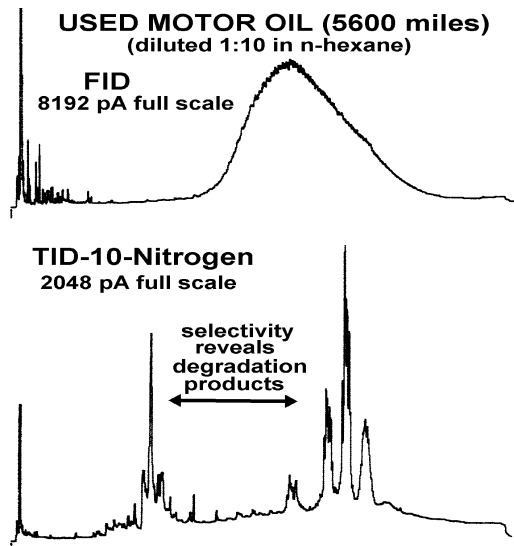


Figure 14. Compared to the mass of unresolved components in the FID chromatogram, TID-10-Nitrogen exhibited peaks corresponding to products of oxidative degradation of the oil. Degradation peaks appear in the oil and their magnitudes build up with miles of usage.

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c.) Glycols & Phenols

Like Acids, Glycols and Phenols are classes of Oxygenates with much larger TID-10 response compared to Alcohols. As a general rule, TID-10 detectivity for Alcohols is in the **low nanogram range** of sample amount; while detectivity for Glycols and Phenols is in the **low picogram range**. Figure 15 illustrates this difference in TID-10 response for a Water sample containing Ethanol, Propylene Glycol, and Ethylene Glycol.

Figure 16 provides a further example of how TID-10 ionization can provide enhanced selective signals for both Glycol and Phenol versus Alcohol sample constituents, as well as demonstrating negligible response to an Aromatic Hydrocarbon component of the sample. In contrast to an FID which requires Hydrogen and Air combustion gases, a TID-10-Nitrogen detection mode uses only Nitrogen as the detector gas and generates Glycol and Phenol responses of magnitudes approaching that of an FID.

Figure 16 also shows that when the detector gas was changed from Nitrogen to Air, TID-10 response to the Glycol compound was diminished while the Phenol response remained prominent.

Figure 17 illustrates the difference in TID-10-Nitrogen response for the oxygenated compound structures associated with Phenol and Anisole.

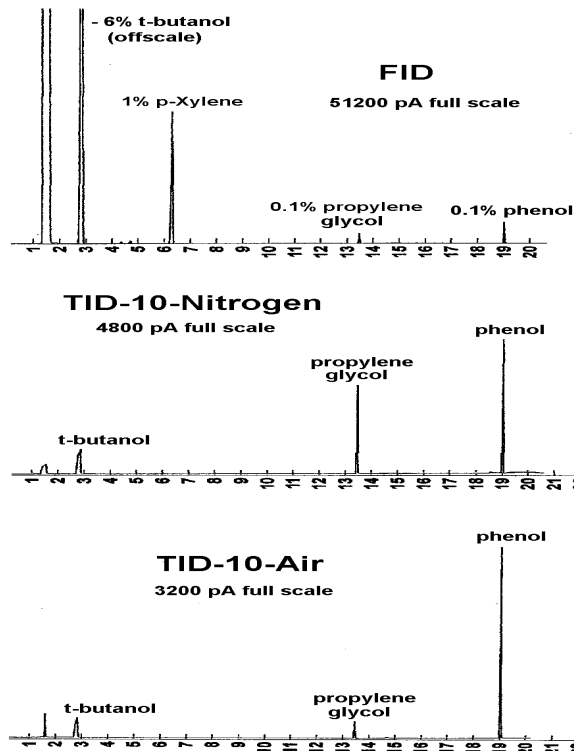


Figure 16

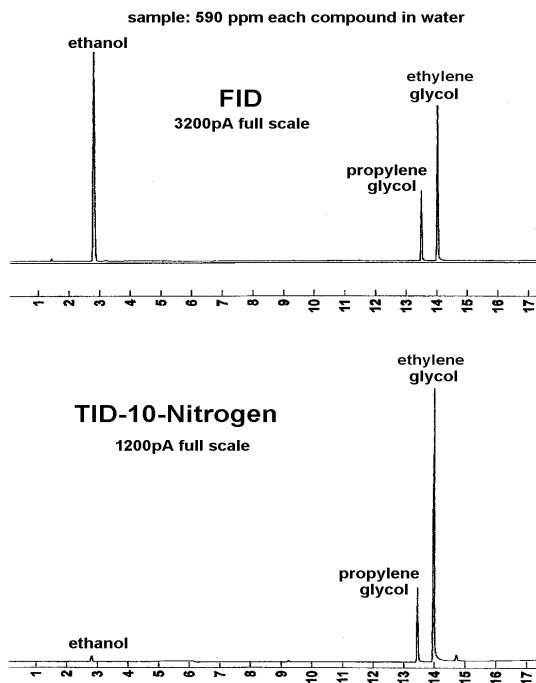


Figure 15.

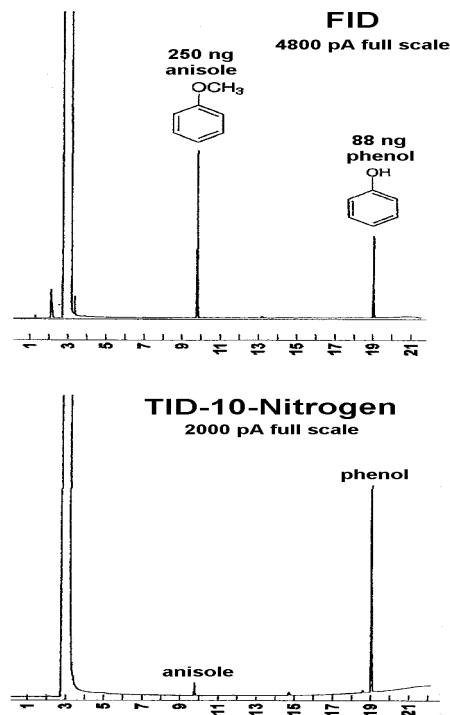


Figure 17.

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The characteristic that TID-10 ionization can provide significant differences in response for one class of Oxygenates versus another is often very useful in the analyses of complex samples. Figures 18 and 19 illustrate analyses of an essential oil sample which consisted of a complex matrix of Hydrocarbon and Oxygenate compounds. Whereas an FID responded to all of these compounds, Figure 18 illustrates TID-10 detection of just the Oxygenates. Furthermore, as shown in earlier data of this report, TID-10 ionization with a detector gas environment of Air rather than Nitrogen provided added selectivity of certain Oxygenates relative to others. Figure 19 demonstrates such TID-1-Air enhanced responses for the Phenolic Antioxidants, BHA and BHT, which are widely used as preservatives in food products.

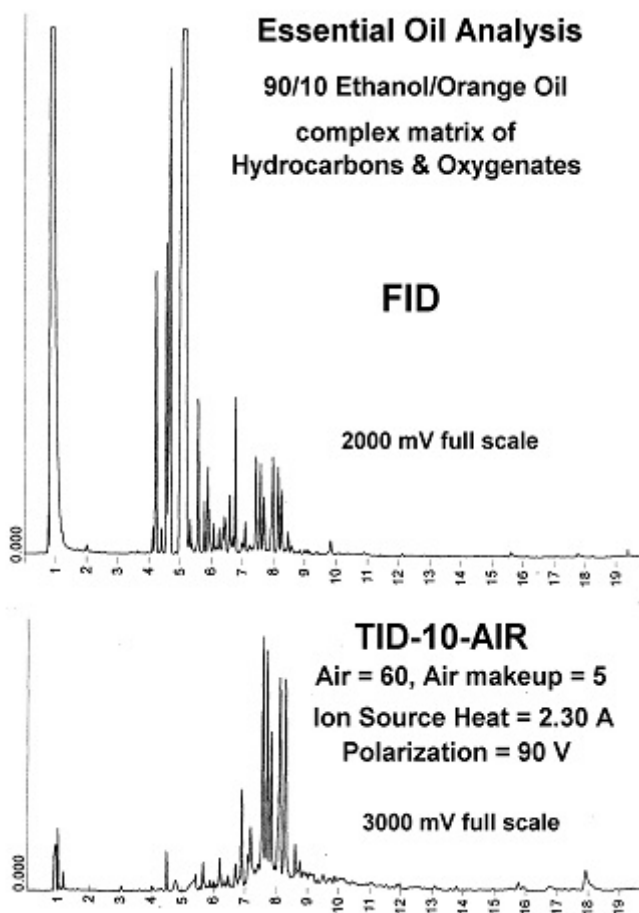


Figure 18. Data obtained on a Thermo Trace Ultra GC fit with a DET Retrofit NPD/TID/CCID/FID Tower and either a Bare Wire Ignitor/Polarizer Probe (FID) or a TID-10 Ceramic Ion Source, with both powered by Thermo's NPD electronics.

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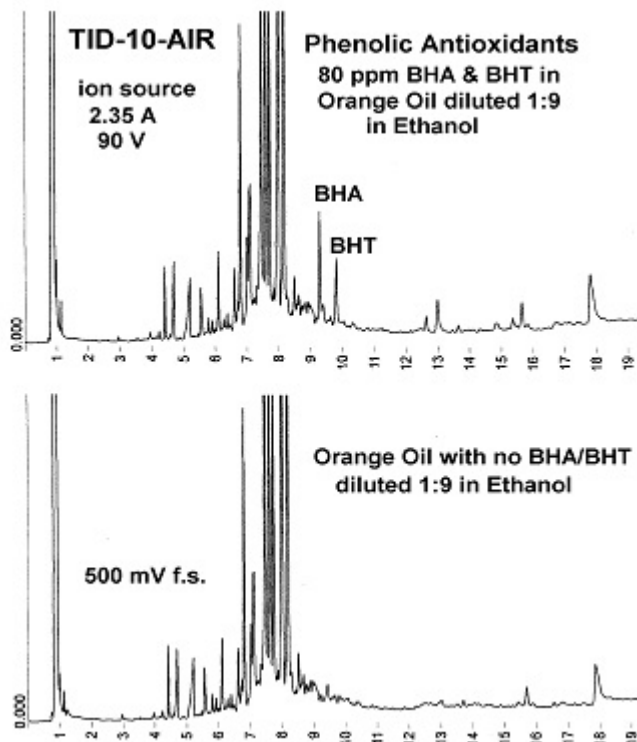


Figure 19.

d.) Flavors & Fragrances.

Many flavor and fragrance compounds contain "O" atoms and are amenable to selective detection using TID-10 ionization. In comparison to FID detection of these types of compounds, TID-10 detection equipment provides the advantages of needing only Nitrogen or Air as the detector gas (i.e., no Hydrogen required), discriminates against compounds that do not contain "O" atoms, and is easily reconfigured to provide alternate selective detection of compounds containing "N" or "P" atoms. Furthermore, TID-10 ionization detection is non-destructive so that aromas of eluting compounds can be sensed at the detector exit, and series tandem configurations with other type detectors are possible to allow 2 simultaneous detector signals from the same sample.

Like the previous discussions of Alcohol, Acid, Glycol, and Phenol compounds, TID-10 ionization of Flavor and Fragrance compounds can provide differences in response magnitudes depending on where the "O" atoms are located in a compound's molecular structure, as well as substantial differences depending on whether Nitrogen or Air is used as the detector gas. FID and TID-10 chromatogram comparisons in Figures 20 and 21 illustrate these differences.

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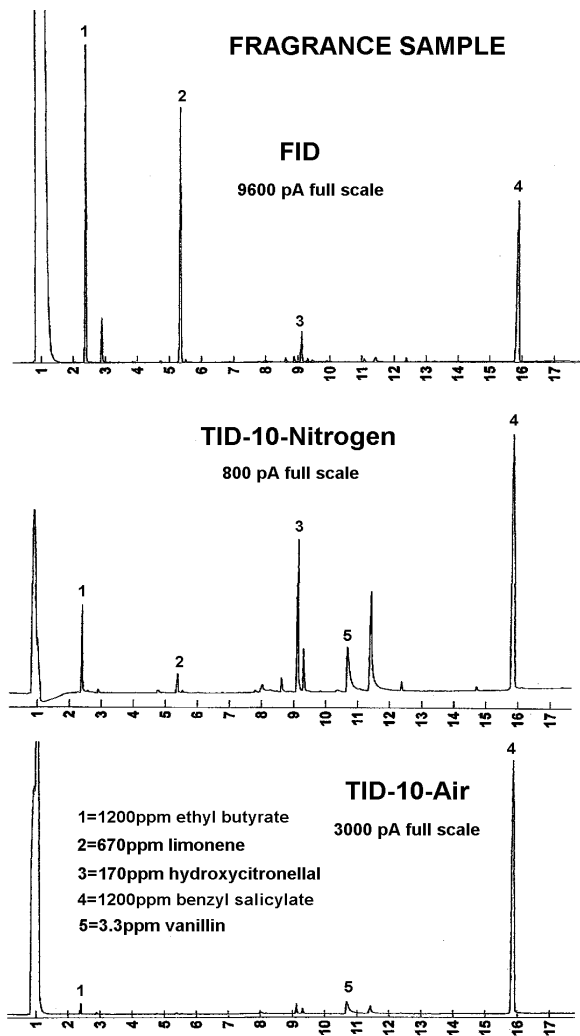
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The fragrance sample analyzed in Figure 20 consisted of a 1:300 dilution in Acetone of a Fragrance Materials Association Mix (Restek #31807). Components and concentrations of the analyzed sample were as follows:

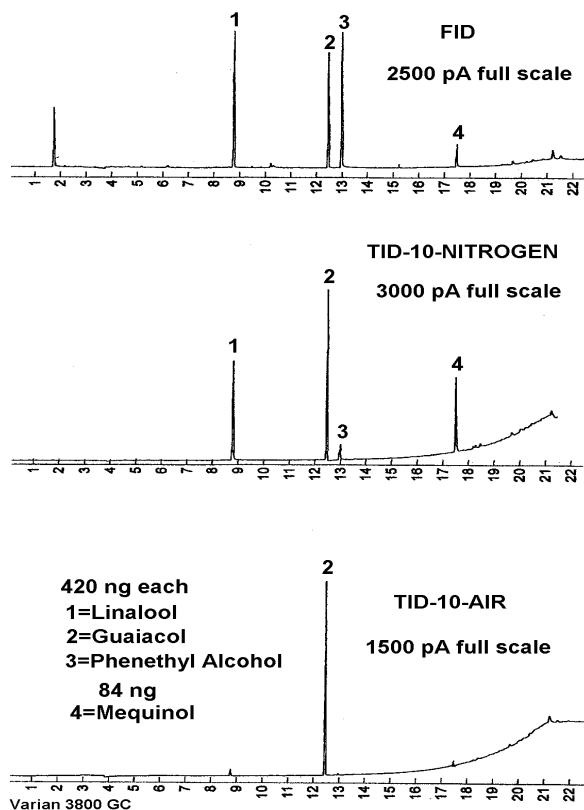
Compound	Concentration (ppm)
ethyl butyrate	1190.00
limonene	666.00
eucalyptol	16.60
benzoic acid	33.30
cinnamic aldehyde	16.60
geraniol	20.00
hydroxycitronellal	166.00
thymol	9.99
cinnamyl alcohol	9.99
vanillin	3.33
cinnamyl acetate	9.99
benzyl salicylate	1190.00

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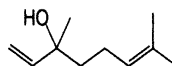
In comparison to FID responses in Figure 20, TID-10 response in Nitrogen diminished the relative magnitudes of the major constituents Ethyl Butyrate and Limonene, while enhancing the relative responses of Hydroxycitronellal, Vanillin, and Methyl Salicylate. Changing to a detector gas environment of Air provided a very large response to Methyl Salicylate relative to all other sample constituents. The small TID-10-Nitrogen response to Limonene demonstrated that some compounds containing only "C" and "H" atoms have a molecular structure which is electronegative enough to produce negative ion signals on impact with the TID-10 surface.



TID-10 DETECTION OF OXYGENATES



Linalool



Guaiacol

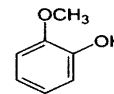
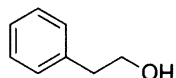


Figure 21

Phenethyl Alcohol



Mequinol

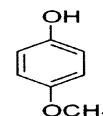


Figure 20

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e.) FAMES & Triglycerides

FAMES and Triglycerides contain "O" atoms and are amenable to TID-10-Nitrogen detection which is a direct surface ionization process. In addition, these classes of oxygenated compounds are characterized by long chains of Methylene (CH₂) functional groups which are amenable to selective detection by the process described as Catalytic Combustion Ionization Detection (CCID). CCID is operative only when the detector gas environment contains Oxygen, and it involves a momentary burst of flame ignition as suitable compounds impact the catalytically active TID-10 surface.

The CCID process selectively detects compounds containing CH₂ groups (i.e., Alkanes, Alkenes, FAMES, Triglycerides, etc.) while having negligible response to Aromatic or Cyclo-Hydrocarbons. The magnitude of CCID response to oxygenated compounds often exceeds the TID-10-Nitrogen response, except there is a threshold in sample amount below which the CCID process drops off

rapidly. Also, the magnitude of CCID response decreases with decreasing concentration of Oxygen in the detector gas. Some comparison of CCID and TID-10-Nitrogen responses have already been provided earlier in this report for other classes of oxygenates.

Another significant characteristic of CCID detection is that it provides larger responses for compounds with saturated Carbon bonds versus compounds with unsaturated Carbon bonds. This saturate vs. unsaturate response difference diminishes with increasing concentration of Oxygen in the detector gas. Hence, in analyses of FAME and Triglyceride samples, TID-10-Nitrogen responds with comparable magnitudes to both saturates and unsaturates; TID-10 with an Air detector gas responds with larger CCID signals for the saturates; and TID-10 with an Oxygen gas environment provides CCID signals with less difference between saturates and unsaturates. These are the general descriptions for the data shown in Figures 22 and 23.

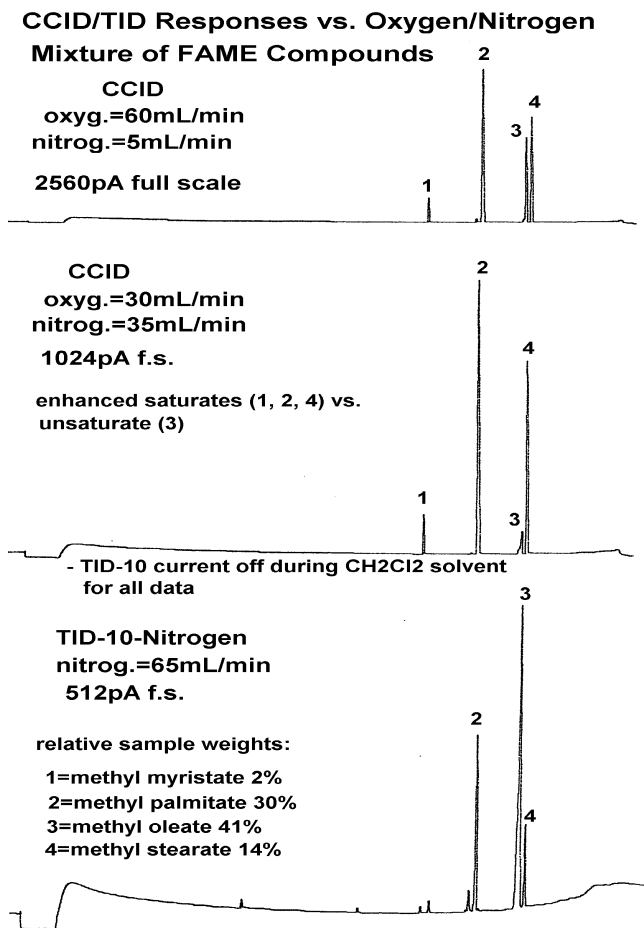


Figure 22. Mix of Saturate & Unsaturate FAMES.

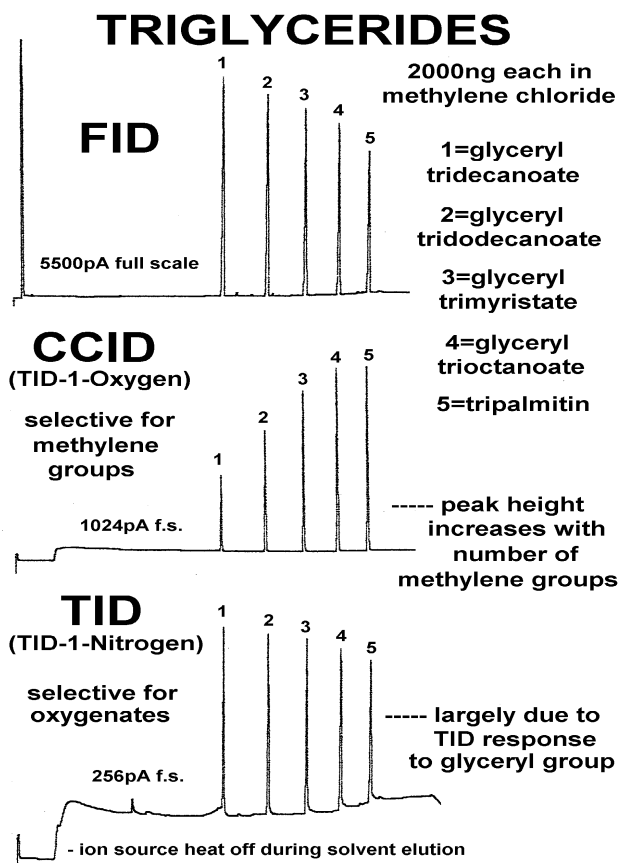


Figure 23. TID-10 ion source is a more robust version of the earlier TID-1 ion source used for these data. TID-10 response is the same. Mix of Saturated Triglycerides.

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3.) RESIDUAL CAFFEINE AND VANILLA FLAVORING IN "DECAFFEINATED" AND "CAFFEINE FREE" TEAS (INTERCHANGEABLE NPD AND TID-10).

Vanillin is one of the most widely used flavor and fragrance component of many different types of products. It is also an oxygenated compound that has an especially large TID-10 ionization response.

Figures 24 and 25 illustrate interchangeable TID-10 and NPD detection of Vanilla Flavoring and Residual Caffeine in "Decaf" and "Caffeine Free" tea samples. The NPD mode provided exceptional sensitivity for the Caffeine and the TID-10 mode provided the selectivity for the Vanilla compounds.

Figures 24 and 25 are examples of the versatility of DET's selective detection technology which features inexpensive ceramic ion sources easily interchanged into the same basic detector equipment. For these tea data, a TID-4 type ceramic ion source was used for the NPD chromatogram because it is formulated to provide the best possible response for N compounds like Caffeine. TID-10 was the ion source choice for selective detection of the Vanilla flavoring compounds. This same equipment combination is applicable to selective detection of many other types of compounds containing "O" or "N" atoms which are the 2 most common occurring heteroatoms in organic chemistry.

TEA Sample - Bigelow French Vanilla Decaffeinated

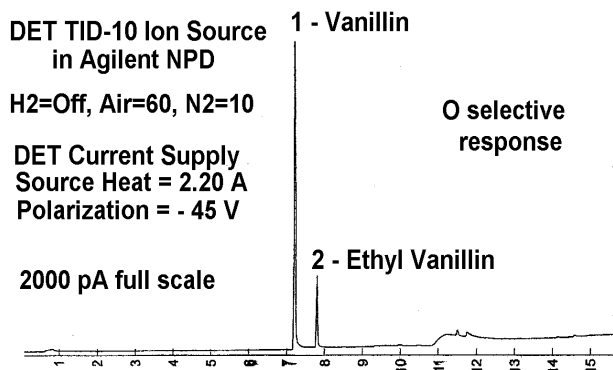
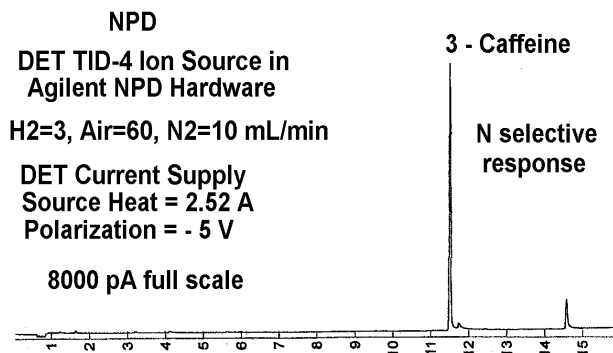
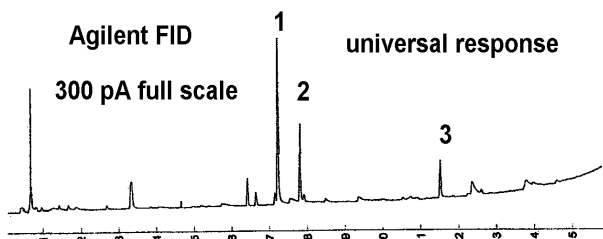


Figure 24.

Tea Sample - Celestial Seasons Sleepy Time Vanilla ("caffeine-free" herbal tea)

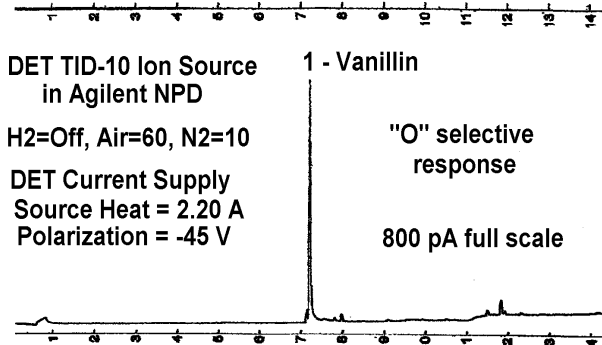
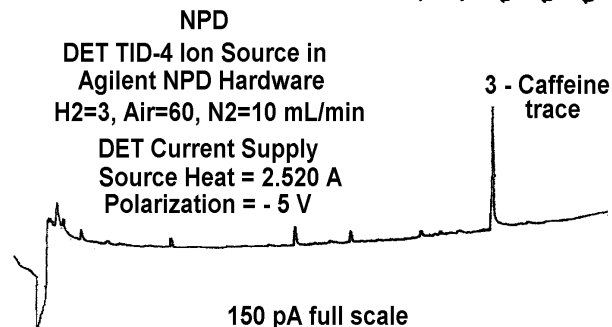


Figure 25