DET REPORT

NO.62 MAY 2010

1.) CATALYTIC COMBUSTION IONIZATION METHOD FOR SELECTIVE DETECTION OF CH$_2$ FUNCTIONAL GROUPS IN PETROLEUM, BIOFUEL, AND FAME SAMPLES INCLUDING DIFFERENTIATION BETWEEN SATURATED AND UNSATURATED CARBON BONDS.

2.) SELECTIVE TID-1 DETECTION IN AN INERT NITROGEN ENVIRONMENT ALLOWS GASOLINE TO BE USED AS AN EXTRACTING SOLVENT.

3.) CRITIQUE OF AGILENT'S INSTRUCTIONS FOR THE 6890/7890 NPD.

1.) CATALYTIC COMBUSTION IONIZATION METHOD FOR SELECTIVE DETECTION OF CH$_2$ FUNCTIONAL GROUPS IN PETROLEUM, BIOFUEL, AND FAME SAMPLES INCLUDING DIFFERENTIATION BETWEEN SATURATED AND UNSATURATED CARBON BONDS.

Recent DET Reports have shown TID-1 surface ionization chromatograms for Petroleum, Biodiesel, and FAME (Fatty Acid Methyl Ester) samples. For the case where the ceramic TID-1 surface is operated in a gas environment containing Oxygen, there is a special category of ionization response that can best be described by the terminology, **Catalytic Combustion Ionization Detection (CCID)**. CCID is not a trace level detection method, but instead applies to nanogram or larger concentrations of organic chemical compounds containing chains of CH$_2$ functional groups. Basically, the CCID process involves a burst of gas phase ionization that occurs as an eluting high concentration organic compound momentarily ignites a flame as it impacts the hot catalytically active TID-1 surface in the presence of Oxygen.

Fatty Acid Methyl Esters (FAMEs) contain long chains of CH$_2$ groups, and they are currently compounds of high analytical interest because of their presence in Biofuels. The last DET Report showed examples of FAME chromatograms using what we now identify as CCI detection. The data from that last report are shown again in Figure 1. The sample analyzed contained both saturated and unsaturated FAME compounds. In contrast to an FID which detected all the FAME components, a surprising discovery was that TID-1 ionization detected mainly only the saturated compounds. With an O$_2$ gas environment, the only unsaturated FAMEs detected were peaks labeled 15, 17, and 37, and with an Air environment the only peaks exhibited in the displayed chromatogram all corresponded to saturated FAMEs.
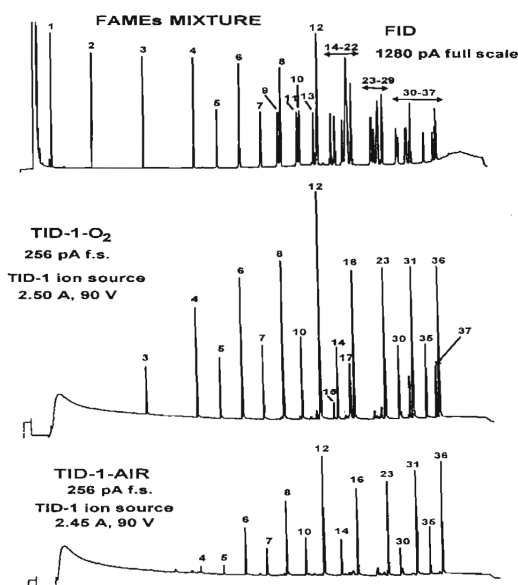

Figure 1. FAME Unsaturates in TID chromatograms:
15=cis-10-Heptadecenoic (C17:1), 2wt%;
17=Oleic (C18:1n9c), 4wt%; **37**=Nervonic (C24:1n9), 2wt%.
Some of the **FAME Saturates**: **12**=Palmitic (C16:0), 6wt%;
14=Heptadecanoic (C17:0), 2wt%; **16**=Stearic (C18:0), 4wt%;
23=Arachidic (C20:0), 4wt%;
30=Heneicosanoic (C21:0), 2wt%; **31**=Behenic (C22:0), 4wt%;
35=Tricosanoic (C23:0), 2wt%; **36**=Lignoceric (C24:0), 4wt%

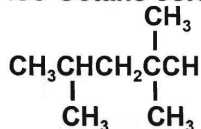1

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Given the observation that a Carbon double bond can significantly reduce the magnitude of response produced by Catalytic Combustion Ionization of CH_2 groups in FAME compounds, a related examination of Alkanes versus Alkenes was undertaken. Figure 2 compares FID and TID-1 chromatograms for a mixture of 1% each of n-Dodecane and 1-Tetradecene in an iso-Octane solvent. Whereas, the FID produced comparable signals for the Dodecane and Tetradecene compounds, the TID-1 chromatograms exhibited a larger signal for the Dodecane, and the ratio of Dodecane to Tetradecene signals increased as the mixture of Nitrogen to Air increased in the detector gas environment.

The TID-1 data in Figure 2 are the result of Catalytic Combustion Ionization of the CH_2 functional groups in the sample compounds. Like the FAMEs, the existence of a Carbon double bond in the Alkene diminished the ionization response even though both the Alkene and Alkane components contained large numbers of CH_2 groups.

Two other characteristics of the Catalytic Combustion Ionization process are evident in Figure 2. First, the comparison of FID and TID-1 responses to the solvent, iso-Octane, demonstrated the large CCID selectivity to compounds containing many CH_2 groups versus a compound like iso-Octane which only has one CH_2 group. Secondly, the Figure 2 data demonstrated that the absolute magnitudes of CCID responses increased with increasing Air (i.e., Oxygen) in the detector gas mix.

SAMPLE CONSTITUENTS FOR FIGURE 2

iso-Octane solvent (O)

$$CH_3CHCH_2CCH$$

(with CH_3, CH_3, CH_3 branch groups)

n–Dodecane (D)

$$CH_3(CH_2)_{10}CH_3$$

1-Tetradecene (T)

$$CH_2=CH(CH_2)_{11}CH_3$$

Alkane vs. Alkene Response Comparison

1% each, n-dodecane (D) and 1-tetradecene (T) in iso-octane (O)
(U = impurity)

- O (offscale)

FID
32800 pA f.s.

- D   - T   U

TID-1
Air=50, Nitr.=10
256 pA f.s.

- D   - T   U   O

TID-1
Air=30, Nitr.=30
128 pA f.s.

- D   U   T   O

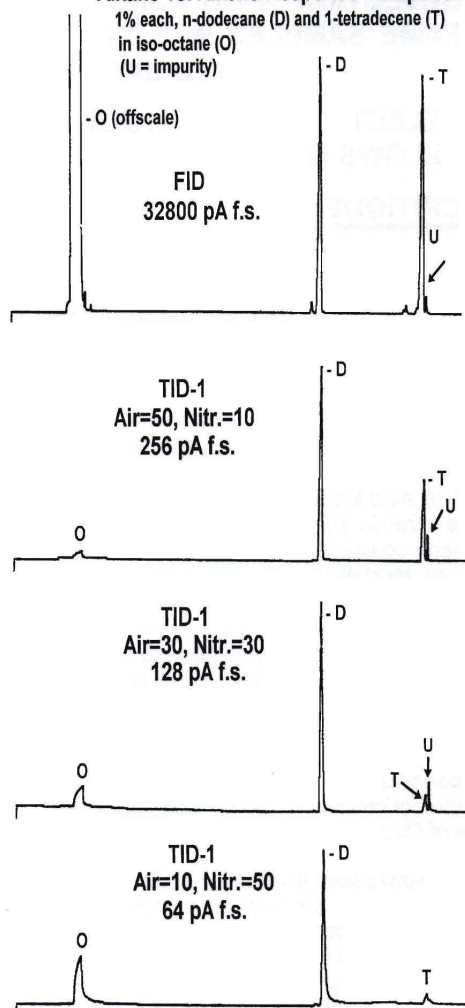TID-1
Air=10, Nitr.=50
64 pA f.s.

- D   T   O

Figure 2. 0.6µL injected. Agilent 6890 GC.
30m x 0.53mm HP-1ms, He=6 mL/min, 50 -160°C at 6°C/min. TID data from Agilent NPD equipment modified with TID-1 ion source powered by a DET Current Supply, and Air/N_2 detector gases (i.e., no H_2). Detector = 320°C.
TID-1 ion source heat =2.30 A, polarization = - 45 V.
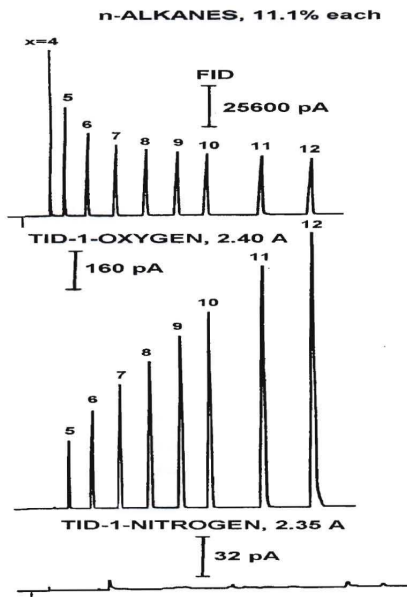
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n-ALKANES, 11.1% each

Figure 3. n–ALKANES, $CH_3(CH_2)_xCH_3$
Varian GC with DET retrofit NPD/TID hardware and stand-alone DET Current Supply.

The response difference between Alkanes and Alkenes diminishes with increasing Oxygen concentration in the detector gases. Figures 3 and 4 show data from mixtures of linear chain Alkane and Alkene compounds for a TID-1 ion source operated in a gas environment of Oxygen rather than Air. In contrast to the FID responses, the TID data in both figures exhibited increasing signal magnitudes as the number of CH_2 groups in the sample compounds increased. For individual Alkane and Alkene compounds with comparable numbers of CH_2 groups, the Alkane responses were consistently higher than the Alkene responses.

CCID provides selectivity for organic compounds containing multiple CH_2 groups versus other type compounds which do not. This is demonstrated in Figure 5 with the analysis of a mixture containing several linear chain Alkanes, two Aromatic Hydrocarbons (i.e., Benzene and Toluene), and 2 branched chain Alkanes (i.e., iso-C_8 and iso-C_{12}) which have only a few CH_2 groups. At the sensitivity displayed, the TID-1-Oxygen chromatogram showed no indication of the Aromatic or Branched Chain constituents.
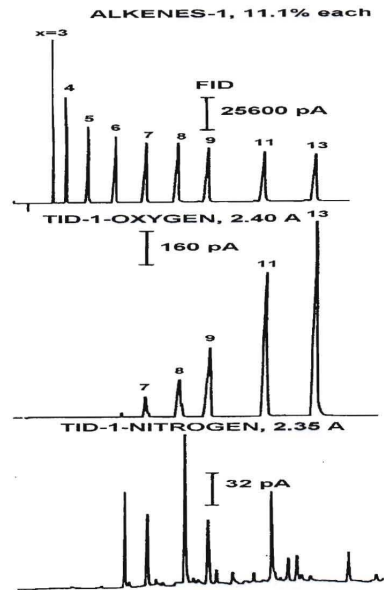
ALKENES-1, 11.1% each

Figure 4. 1-ALKENES, $CH_2=CH(CH_2)_xCH_3$

1= 1.1% Ethanol
2=11.1% n-C_6
3=11.1% Benzene
4= 9.1% iso-C_8
5=11.1% Toluene
6=11.1% n-C_8
7=11.1% iso-C_{12}
8=11.1% n-C_{12}
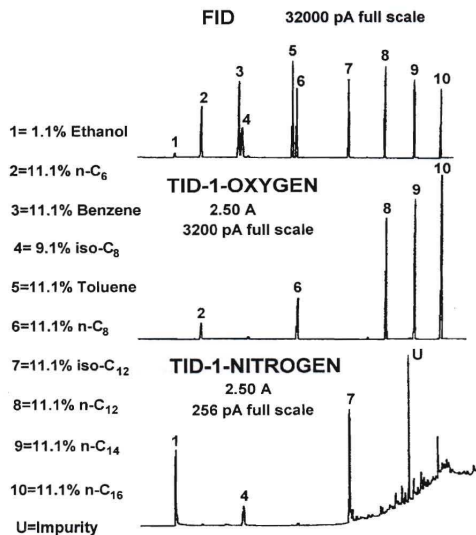9=11.1% n-C_{14}
10=11.1% n-C_{16}
U=Impurity

Figure 5. 0.1µL injection of sample mixture. Varian GC, DET retrofit hardware and DET Current Supply.

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Catalytic Combustion Ionization Detection requires that there be a sufficient concentration of an eluting fuel compound to ignite a momentary flame. Practically, this means that there is a concentration threshold for sample compounds below which the response drops off sharply. This is well illustrated by the graph in Figure 6. On this type of graph, linearity of response is indicated by a horizontal line as shown for the Oxygenate compound, Diethyl Phthalate. In contrast, the response to n-C_{16} decreased sharply below a sample amount of about 200 ng. For any given combustible fuel compound, the concentration level at which this threshold occurs depends on such things as the number of CH_2 groups in the compound, the temperature of the ceramic ignition surface, and the amount of Oxygen in the detector gas environment. The ignition threshold will shift toward lower sample amounts with increasing CH_2, temperature, and Oxygen.

Figure 7 demonstrates how Catalytic Combustion Ionization can provide uniquely simplified analyses for certain types of constituents in complex sample matrices like Gasoline. In the bottom chromatogram of Figure 7, the detector gas environment was mainly Air, and the TID-1 ion source was at a relatively low surface temperature in the range of 300 - 400°C which was sufficient to ignite combustive oxidation of the CH_2 groups in n-C_8, n–C_9, and n-C_{10}. Ethanol does not

contain sufficient CH_2 groups for combustion ignition, so its TID-1 signal in Figure 7 can be attributed to a direct thermionic surface ionization process which is known to be responsive to Alcohols and other Oxygenated compounds. The middle chromatogram of Figure 7 demonstrates how a higher temperature for the TID-1 ceramic surface, and a gas environment of Oxygen versus Air, can result in combustive ionization of additional selected constituents of the gasoline. We have not yet identified the additional peaks, but it is unlikely any are due to Aromatic Hydrocarbons.
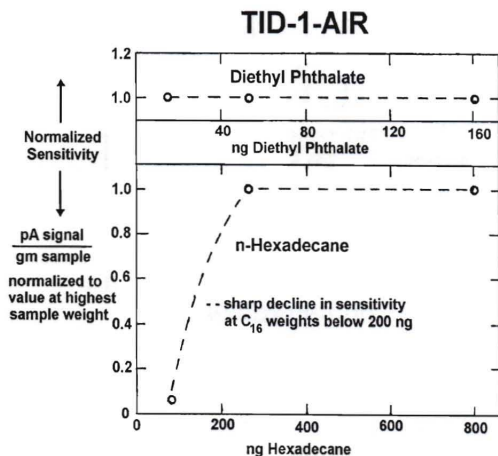
GASOLINE (Chevron, No. Calif., 1/10)

FID
Hydr.=25 mL/min
Air=250 mL/min
Nitr.=10 mL/min

131,000 pA f.s.

TID-1 Ion Source
heat=2.40 A
polariz.= - 45 V

Oxy.=60 mL/min
Nitr.=5 mL/min

256 pA f.s.

TID-1 Ion Source
heat=2.10 A
polariz.= - 45 V

Air=60 mL/min
Nitr.=5 mL/min

8 pA f.s.

TID-1-AIR

Normalized Sensitivity

Diethyl Phthalate

ng Diethyl Phthalate

$\frac{pA\ signal}{gm\ sample}$ normalized to value at highest sample weight

n-Hexadecane

- - sharp decline in sensitivity at C_{16} weights below 200 ng
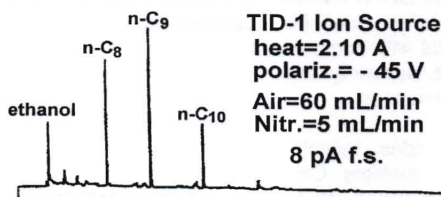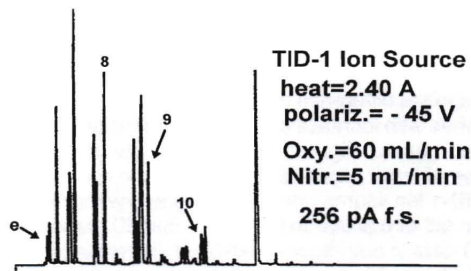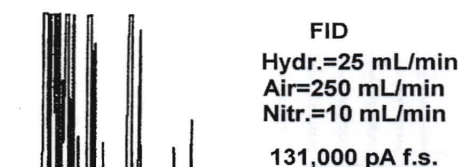
ng Hexadecane

Figure 6. Graph of normalized sensitivity vs. sample weight. Sensitivity=pA of peak height divided by gm of sample weight. Sensitivity data normalized by dividing by the sensitivity corresponding to the highest sample weight.

Figure 7. 0.6µL Gasoline injected neat. Agilent 6890 NPD equipment modified with DET TID-1 ion source and DET stand-alone Current Supply.

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We have used the term"Catalytic" in describing the Combustion Ionization process discussed in this report. That is because the chemical composition of the hot ceramic surface has a significant affect on combustion ignition of fuel constituents. This is demonstrated in Figure 8 where data from a TID-1 ceramic ion source and a CFID type ceramic ion source are compared. The top 2 chromatograms of this figure were generated by heating both ion sources with the same magnitude electrical current. Since both were of comparable physical size, comparable heating currents meant comparable surface temperatures. It is clear from these data that the CFID source produced no combustion ionization signals like those from the TID-1 source. Only when the surface temperature of the CFID source was increased substantially did the combustion ionization signals shown in the bottom chromatogram appear. In this case of a very hot CFID source, many gasoline constituents were ignited in combustion, and the resulting chromatogram had many similarities to that of an FID chromatogram. Amongst the different type ceramic ion sources currently manufactured by DET, TID-1 and CFID represent the 2 extremes with regard to their catalytic/ionization activity.

Figure 9 demonstrates Catalytic Combustion Ionization Detection for a Diesel Fuel sample. In an Air environment, only the linear chain Alkanes were detected, while an Oxygen environment produced some responses for underlying constituents as well.

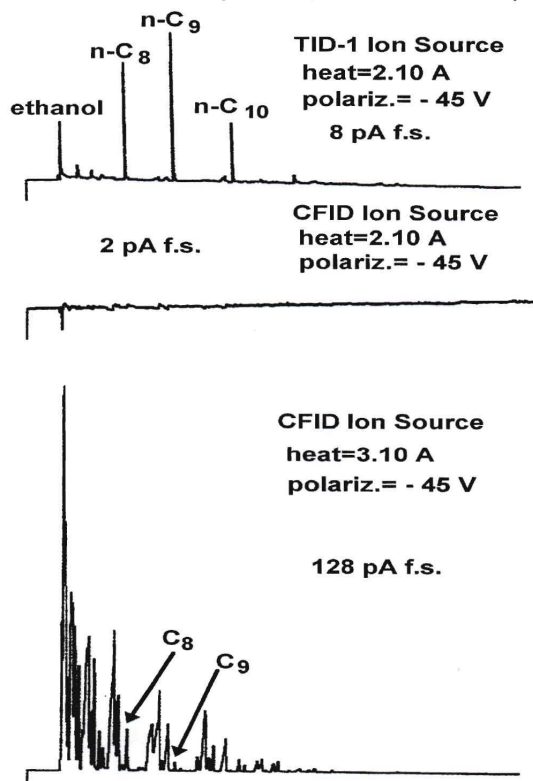**Figure 8.** Same Gasoline sample and equipment as Figure 7, except interchange of TID-1 and CFID type ceramic ion sources.
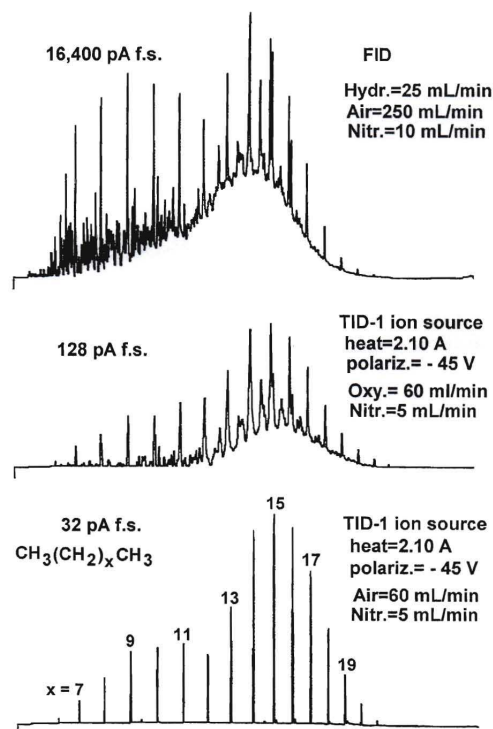
Figure 9. 0.2µL Diesel Fuel injected neat. Same Agilent and DET equipment as Figure 7.

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There is currently high interest in chemical analyses of Biofuel samples, and Catalytic Combustion Ionization Detection can provide some unique selectivities for these complex samples. Figures 10 and 11 illustrate analyses of B20 and B100 Biofuel samples obtained from AccuStandard (New Haven, CT). In contrast to the "neat" Diesel fuel sample of Figure 9, these B20 and B100 samples were 20 mg/mL dilutions of each in a Methylene Chloride solvent. With the diluted samples, good selectivity for CH_2 functional group compounds was obtained even with an Oxygen gas environment in the detector. In these chromatograms, the peaks labeled "Cx" corresponded to linear chain Alkanes, and the peaks labeled "Fx" corresponded to FAME compounds. In the FID chromatogram of the B20, the peak region labeled F17-F22 was a group of unresolved FAME unsaturates, and the TID-1-O_2 chromatogram showed

that peak F17 (Oleic Acid Methyl Ester) was the dominant member of that group. The other FAME components, F12 and F16, were the saturated FAME compounds, Palmitic and Stearic, respectively. Similar comments apply to the B100 analysis.

In addition to chemical detection applications, this work with Catalytic Combustion Ionization has revealed several factors relating to the general science of fuel combustion ignition. These are as follows:
1.) Increased catalytic activity of a heated ceramic surface lowers the temperature required for ignition;
2.) High temperature oxidation of CH_2 groups is an important process in the ignition of fuels; and
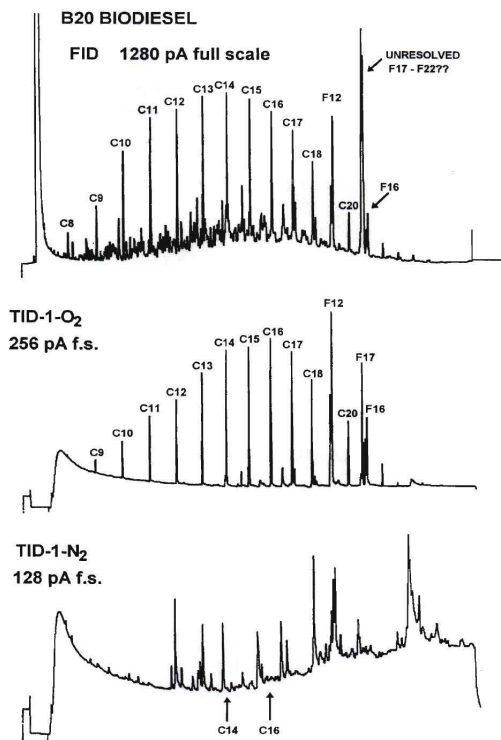3.) Compounds with saturated Carbon bonds ignite in combustion more easily than compounds with Carbon double bonds.

Figure 10. 0.7µL injected. 20mg/mL B20 in Methylene Chloride. Thermo Scientific Trace GC with DET NPD/TID detector hardware and Thermo's NPD electronics.
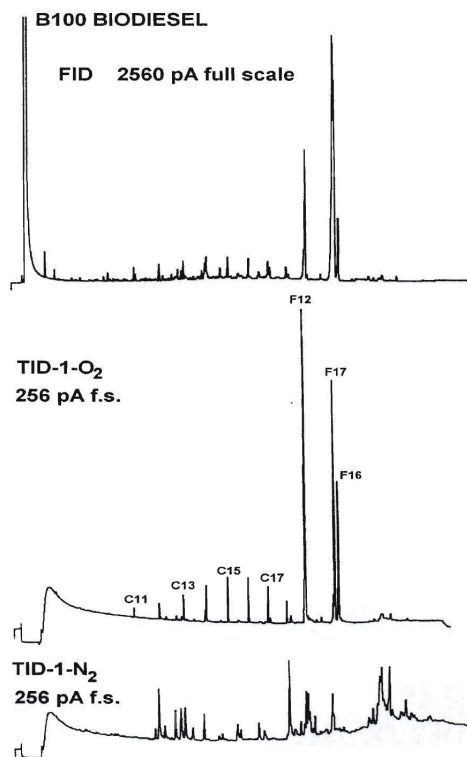To minimize upset from the Chlorinated solvent, TID-1 heat was turned OFF during first 2 minutes of the run.

Figure 11. 0.7µL injected. 20mg/mL B100 in Methylene Chloride. Same equipment as Figure 10.

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2.) SELECTIVE TID-1 DETECTION IN AN INERT NITROGEN ENVIRONMENT ALLOWS GASOLINE TO BE USED AS AN EXTRACTING SOLVENT

Several of the figures earlier in this report included TID-1 chromatograms generated with inert Nitrogen instead of an oxidizing detector environment. In an inert gas environment, TID-1 detection is due to a Thermionic Surface Ionization process that provides the best selectivity versus Hydrocarbon interferences. In past DET Reports, the analysis of Ethanol in Gasoline has served as a signature chromatogram illustrating how a selective detector can greatly simplify the selective detection of Oxygenates in a complex Hydrocarbon matrix.

Unlike the Catalytic Combustion Ionization process, the TID-1-Nitrogen surface ionization is a process capable of detecting trace level sample constituents that are otherwise not revealed by other detection techniques. For example, the Alkene standards used for Figure 4 of the previous section contained numerous heteroatom impurities that were displayed in the TID-1-Nitrogen chromatogram. Similarly, the TID-1-N_2 chromatograms in Figures 10 and 11 revealed numerous peaks at retention times unrelated to the labeled Cx and Fx peaks in the other chromatograms of these B 20 and B 100 Biofuel samples.

In analyzing Gasoline samples with the TID-1-Nitrogen mode, we found that consideration needed to be given to the material of the gasoline storage container. Figure 12 compares TID-1-N_2 chromatograms for the same Gasoline sample stored in a glass vial versus storage in a red colored HDPE container commonly used for small scale gasoline transport by consumers. The HDPE chromatogram clearly revealed the buildup of extraneous peaks extracted from the container material. By contrast, the FID chromatogram of that same HDPE sample showed no evidence of the extraneous peaks. This was a good example demonstrating that selectivity of TID-1-Nitrogen detection allows Gasoline to be effectively used as an extracting solvent. For a general detector like an FID, Gasoline would be a ridiculous choice for an extracting solvent because of the many interfering peaks. Gasoline storage and transport is, of course, a huge endeavor all over the world, and selective detection is an easy way of monitoring composition changes caused by compounds originating in the containment vessel.

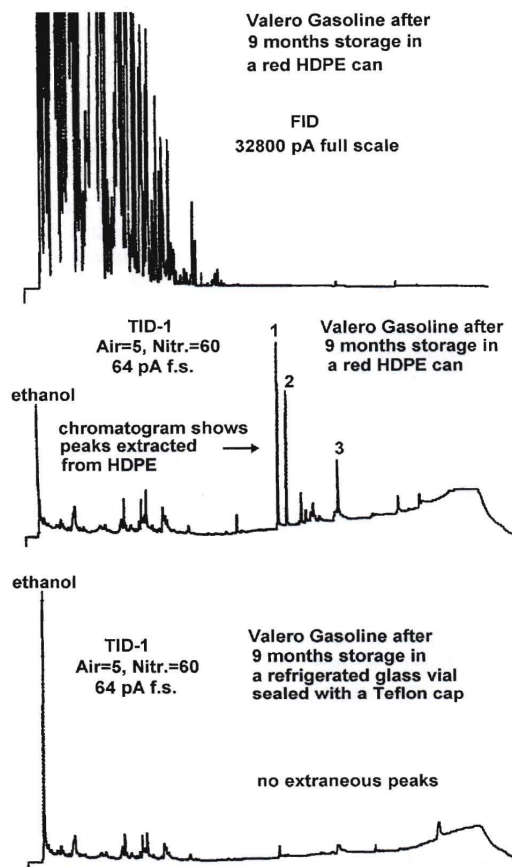**Gasoline Extraction of Storage Container Constituents**

Valero Gasoline after 9 months storage in a red HDPE can

FID 32800 pA full scale

TID-1 Air=5, Nitr.=60 64 pA f.s.

ethanol

Valero Gasoline after 9 months storage in a red HDPE can

chromatogram shows peaks extracted from HDPE

ethanol

TID-1 Air=5, Nitr.=60 64 pA f.s.

Valero Gasoline after 9 months storage in a refrigerated glass vial sealed with a Teflon cap

no extraneous peaks

Figure 12. Agilent 6890 NPD equipment modified with a DET TID-1 ion source powered by a stand-alone DET Current Supply.

3.) CRITIQUE OF AGILENT'S INSTRUCTIONS FOR THE 6890/7890 NPD

We recently downloaded the latest version of Agilent's User Guide for the 7890 NPD, and were dismayed that some of the instructions are not consistent with the science of the detection process. Based on our 30 plus years experience with NPDs, and long term usage of the 6890 NPD, we offer the following contrasting viewpoints.

Two Most Important NPD Operating Parameters.
The NPD is basically a very simple detector consisting of an electrically heated ion source (bead), a nearby collector electrode, and a detector gas environment comprised of a dilute mixture of Hydrogen in Air. NP response turns on when the ion source is heated sufficiently to ignite the H_2 - Air mixture, and the H_2 flow is low enough that the ignited chemistry remains as a boundary layer about the ion source rather than flashing back to form a self-sustained flame at a jet structure. The 2 most important parameters are maintaining the H_2 flow at a value of 5 mL/min or less, and determining what magnitude of Bead Voltage is required to heat the ion source to ignition temperature.

Overemphasis on the Magnitude of Detector Background Signal (Offset) at Chemistry Ignition.
As Bead Voltage is slowly increased, NP chemistry ignition is indicated by a sudden increase in the detector background signal. The magnitude reached by the background signal at the point of ignition will vary from one ion source to another, and it also depends on the magnitude of the H_2 flow, on any column bleed, and on the age of the ion source. Therefore, the most reliable means of establishing NP detection is identifying what magnitude of Bead Voltage is required for the sudden increase in background signal, rather than trying to attain a certain predetermined level of background signal.

Flaws in the Concept of Agilent's Adjust Offset.
NPDs are unlike most other GC detectors in that the absolute magnitudes of sample response, background signal, and noise can be varied over a wide range by adjustments in Bead Voltage and H_2 flow. Since large signal magnitudes can be accompanied by large noise magnitudes, an NPD user needs to always consider signal-to-noise rather than just absolute signal size. As ion sources age, it is not uncommon that absolute signal magnitudes decay with time. However, the noise also decays with time, so signal-to-noise is more constant.

Agilent's Adjust Offset was conceived as a means of correcting for the decay in absolute signal magnitudes by electronically increasing the Bead Voltage to increase the ion source temperature. The problem is that ion source activity decays at an even faster rate as its temperature increases, so that the Adjust Offset feature actually contributes to shortening the operating life of the ion source.

A second flaw with the Adjust Offset concept is that it requires some predetermined magnitude of background signal to be inputted as the target level for the automatic adjustments of Bead Voltage. It is unrealistic to expect that the same target level is appropriate for all ion sources at all points of time in their operating life. The result is that Adjust Offset invariably leads to operating ion sources hotter than they need to be to ignite the NP chemistry, and that further leads to shorter operating life.

Agilent's "Dry Bead" Instruction.
What's this all about? We have processed tens of thousands of ceramic ion sources on the 6890 NPD and have never been concerned about "drying the bead". We can only surmise that this instruction is a remedy for some quirk associated with Agilent's automatic Adjust Offset process being affected by extraneous signals caused by moisture adsorbed on ceramic insulators in the detector rather than on the bead.

NPD Jet Selection.
The NPD is not like an FID where a self-sustained flame burns at the jet, so what is the point of having a selection of different size jet orifices? The only function of the jet in an NPD is that it is a convenient way of routing the GC column, and Hydrogen and Makeup gas flows into the detector volume. For years, we have used a wide bore jet purchased from Agilent that allows fused silica columns of 0.53mm dia or smaller to be inserted clear through the jet to a location in close proximity to the ion source. This eliminates any possible sample degradation on the interior metal of the jet, eliminates any clogging of the jet orifice from complex sample matrices, and eliminates the need to ever replace the jet. Contact DET for more advice on NPD jets.

Solvent Quenching.
Passage of a solvent through the NPD may sometimes quench the NP chemistry, and it does not reignite. This is simply a consequence of the Bead Voltage needing to be a little higher. If the Bead Voltage is sufficient for chemistry reignition, then it does not matter whether the NPD background level is 3 or 30pA.