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NO.67 MARCH 2013

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4.) **FAME AND TRIGLYCERIDE RESPONSES VS. DETECTOR OXYGEN.**

1.) CATALYTIC COMBUSTION IONIZATION DETECTION (CCID) - ESSENTIAL REQUIREMENTS FOR THIS UNIQUE SELECTIVITY OF CH_2 GROUPS.

The Catalytic Combustion Ionization technique of chemical detection (CCID) involves ignition of a momentary burst of flame ionization as an organic sample compound impacts a heated, ceramic ion source. Due to the unique catalytic activity of the ion source ceramic, compounds containing chains of Methylene (CH_2) functional groups are preferentially ionized. Such detectable compounds include Alkane and Alkene Petroleum Hydrocarbons, as well as Fatty Acid Methyl Esters (FAMEs) and Triglycerides. In addition to the catalytic ceramic, other essential requirements for CCID are a sample concentration sufficiently high to provide fuel for the flame ignition, and a detector gas environment containing Oxygen.

The equipment required for CCID is a simple modification of equipment commonly available for Nitrogen Phosphorus Detection (NPD). The most optimum configuration is depicted in Figure 1, and consists of a cylindrical ion source positioned on the axis of a concentric ion collector cylinder. This is the configuration used in the Agilent 6890/7890 NPD, in the Thermo Trace 1300 NPD, and in all DET retrofit detector hardware for other model GC instruments.

An NPD generally uses H_2, Air, and Nitrogen Makeup gases for the detector. In converting to CCID, these 3 detector gas inputs are instead connected to Air or Oxygen gas supplies, along with the possible addition of Nitrogen as a further diluent of the Oxygen concentration.

The catalytic ceramic ionizing element in the CCID has a wire core that allows it to be electrically heated and polarized at a negative voltage relative to the collector.
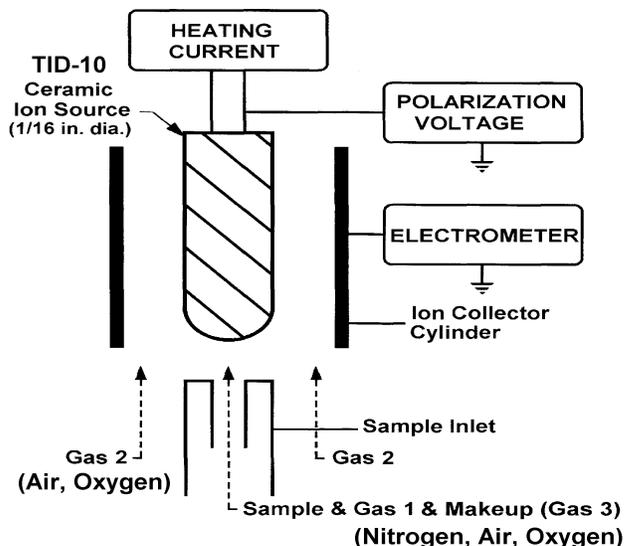
CATALYTIC COMBUSTION IONIZATION

Figure 1. Catalytic Combustion Ionization Detector equipment.

Whereas an optimum NPD polarization is generally a low value of about 4 V, optimum CCID response requires a polarization of 45 V or greater. NPD electronics on Thermo GC models provides this higher voltage capability, and a stand-alone DET Current Supply is available for use with other GC models.

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Initially a TID-1 type ceramic composition was found to be most effective at achieving the CCID selectivity. A more recent TID-10 ceramic provides the same CCID characteristics and is more robust than the TID-1 formulation. The Figure 2 comparison of Gasoline analyses demonstrates that the high catalytic activity of TID-1 and TID-10 ceramics is essential for achieving CCID selectivity. By comparison, the CFID ceramic ion source in Figure 2 had a much lower level of catalytic activity. The special significance of TID-1 and TID-10 ceramics is that they are catalytic surfaces that can initiate combustion of fuel constituents at relatively low temperatures of 300 - 400° C, and that combustion ignition is the result of preferential oxidation of CH_2 groups.

CCID requires a sufficient amount of a sample compound to provide fuel for flame ignition, so it is a chemical detection technique that applies to relatively high sample concentrations. Accordingly, CCID responses are characterized by a threshold in sample amount below which the response drops off rapidly. This is shown in the graph of Figure 3 where it can be seen that the threshold for n–Hexadecane occurred at about 200 ng. The threshold depends on the number of CH_2 groups in the sample compound, on the Oxygen content of the detector gases, and on the temperature of the catalytic surface. Higher numbers of CH_2 groups, Oxygen concentration, and surface temperature all result in a lower threshold in the sample amount needed for CCID onset.
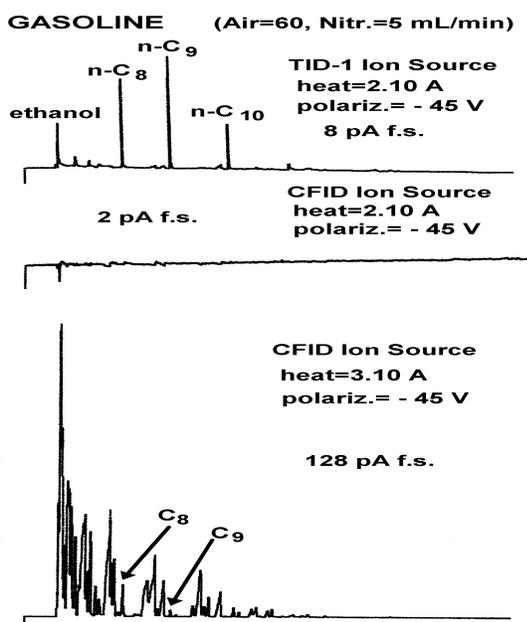

Figure 2. Gasoline analyses comparing a TID-1 ceramic ion source of high catalytic activity vs. a CFID ceramic of low catalytic activity. At a surface temperature comparable to TID-1, CFID produced no signal. At a high surface temperature, CFID response was not very selective.
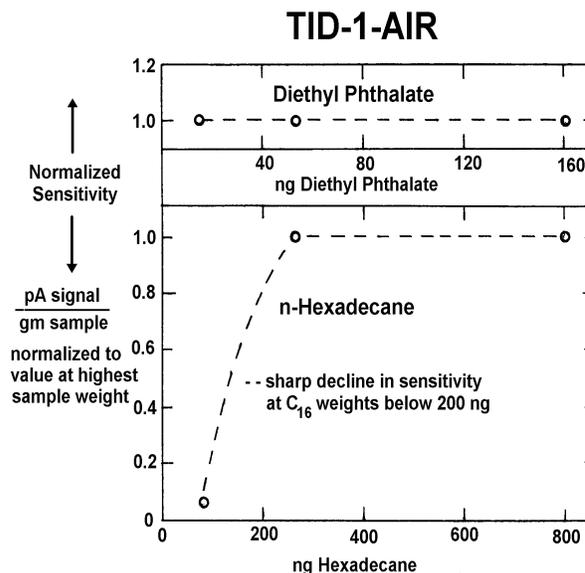
Figure 3. Graph of normalized sensitivity vs. sample weight. Phthalate data represent a TID process involving selective detection of Oxygenated compounds, whereas Hexadecane data represent the CCID process involving selective detection of Methylene groups.

2.) CCID RELATIVE RESPONSES TO DIFFERENT CLASSES OF HYDROCARBONS AS THE OXYGEN CONCENTRATION IN THE DETECTOR GAS IS CHANGED.

Although CCID provides general selectivity to compounds containing CH_2 functional groups, there can be significant response differences for different classes of such compounds depending on whether they also contain double or triple bonded Carbon atoms, or also branched Methyl (CH_3) groups. The magnitude of those response differences depends on the concentration of Oxygen in the detector.

Figure 4 shows a comparison of FID, CCID (TID-10-O_2), and TID-10-Nitrogen chromatograms of a sample containing mixed classes of Hydrocarbons. The constituents of this sample included a Cyclo-Hydrocarbon (peak 1), Branched Alkanes (peaks 2, 3, and 8), Linear Chain Alkanes (peaks 4 and 6), an Alkene (peak 7), and an Alkyne (peak 5). In Figure 4, CCID detection did not respond to the

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Cyclohexane (1), two iso-Octanes (2,3), or the 1-Decyne (5) components of the sample, but did respond to the n–Octane (4), n–Dodecane (6), 1- Tetradecene (7), and Phytane (8) components which all contained large numbers of CH_2 groups. The lack of CCID response to 1-Decyne is interesting because this compound also has a large number of CH_2 groups. However, the existence of a triple bonded Carbon atom in the 1-Decyne structure appeared to inhibit the catalytic combustion ignition of that compound. Conversely, 1-Tetradecene and n–Dodecane with double and single bonded C atoms, and similar large numbers of CH_2 groups, exhibited good CCID response for the conditions used in Figure 4. The detector gases for the CCID data of Figure 4 consisted of 60 mL/min Oxygen and 5 mL/min Nitrogen.

Figure 5 shows how the CCID response to different classes of Hydrocarbons changed as the detector Oxygen was decreased from the concentration of Figure 4. With decreasing Oxygen, the responses of 1-Tetradecene (Alkene peak 4) and Phytane (Branched HC peak 5) decreased relative to the response of n–Dodecane (Linear Alkane peak 3). At the lowest Oxygen concentration shown,

the Alkene response had virtually disappeared and an impurity peak near its retention time was now quite evident. **Hence, with the CCID process, judicious adjustments of the Oxygen concentration in the detector gases provides a means of achieving further selective detection of Linear Alkanes versus Alkenes and Branched Hydrocarbons.**

Also at the lowest Oxygen concentration, the response to n–Octane (Linear Alkane peak 2) had disappeared from the chromatogram. In this case with the lower Oxygen, there weren't sufficient numbers of CH_2 groups in the Octane molecule to initiate the combustion ionization process. **Hence, another characteristic of the CCID process is that by increasingly diluting sample mixtures, and by judiciously adjusting the Oxygen, even Linear Alkane peaks can be selectively removed from a complex CCID chromatogram, with those compounds with the lowest number of CH_2 groups being the first to disappear.**
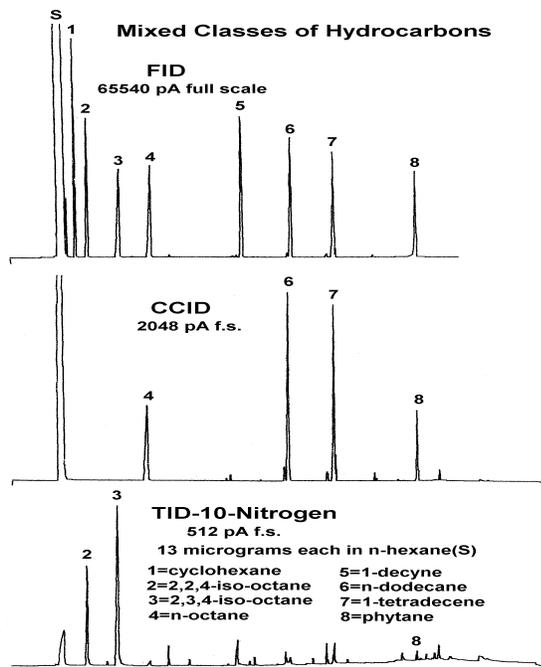

Figure 4. Mixed sample of different classes of Hydrocarbon compounds. Detector gases were 60mL/min O_2 and 5mL/min N_2 for CCID, and 65mL/min N_2 for TID-10-Nitrogen mode. Agilent 6890 NPD equipment with DET TID-10 ion source powered by a stand-alone DET Current Supply at -45 V ion source polarization.
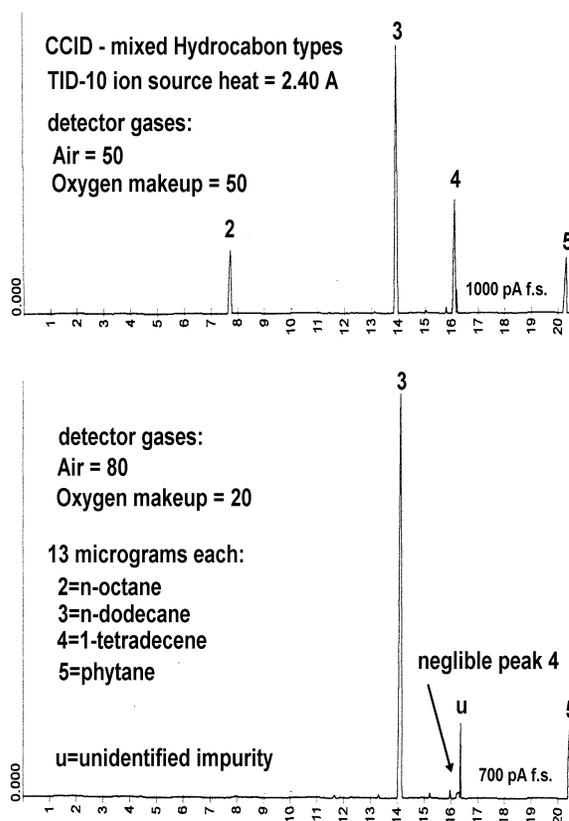

Figure 5. Same sample as Figure 4, but with different peak labels for the Linear Alkane, Alkene, and Branched Alkane components.

3.) VARIATIONS IN DETECTOR OXYGEN CAN ADJUST THE NUMBER AND TYPE OF SELECTED COMPOUNDS DETECTED IN CCID ANALYSES OF PETROLEUM SAMPLES (ALKANES VS. ALKENES, LINEAR VS. BRANCHED HYDROCARBONS).

Figure 6 shows comparative analyses of a commercial Gasoline sample using CCID selective detection versus a universal detection mode identified as Hot Wire Combustion Ionization (HWCID). These data were generated using Thermo Trace Ultra NPD equipment retrofitted with DET NPD/TID/FID detector hardware and powered with the Thermo NPD electronics.

For the HWCID data, detector gases were Hydrogen = 10, Air = 200, and Air Makeup = 50 mL/min, and the ionizing element was a Bare Wire Probe heated to 2.90 A and polarized at - 90 V relative to the ion collector. The concept of HWCID detection is that it maintains ignited flame-like chemistry in the vicinity of the heated wire, but the high total detector gas flow prevents that chemistry from flashing back to form a self-sustained flame at the point in the detector where the H_2 and Air first mix. HWCID is a means of generating FID-like universal detection without requiring that the hardware is equipped with a flame jet structure. Also,. HWCID allows universal detection signals to be obtained from NPD equipment where the H_2 flow is restricted to lower values than typically required for a conventional FID. Compared to an FID, HWCID signal magnitudes are about 100 times smaller, and the HWCID provides about a factor of 2 enhancement of signals from Aromatic Hydrocarbons versus other Hydrocarbon classes.

For the CCID data, detector gases were Air = 50 and Oxygen Makeup = 50 mL/min, and the ionizing element was a TID-10 ceramic electrically heated to 2.40 A and polarized at - 90 V. Figure 6 demonstrates that CCID effectively revealed the presence of Linear Chain Alkanes in the complex Gasoline matrix, whereas these compounds were otherwise masked by the hundreds of other constituents in the universal detector chromatogram. For Figure 6, the sample was a Valero Premium Grade Gasoline and the CCID data showed a different pattern of Linear Alkane peaks than that shown previously in Figure 2 for a sample of Chevron Regular Grade Gasoline. Hence, CCID Linear Alkane fingerprint chromatograms provide an easy way to distinguish between Gasolines from different suppliers, as well as different grades from each supplier.
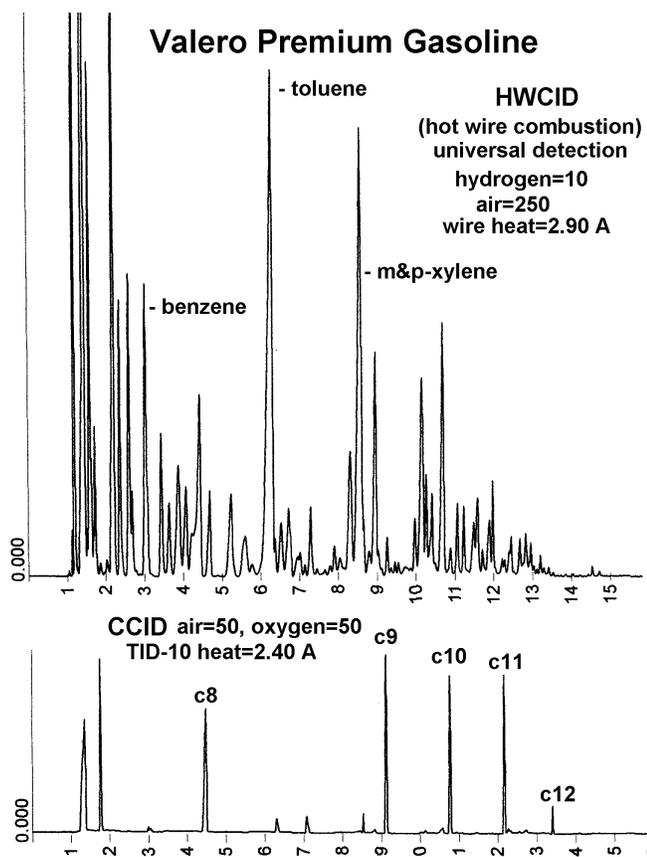
Figure 7 shows how judicious increases in the detector Oxygen concentration can further characterize Gasoline samples by adding Alkene and Branched Hydrocarbon peaks to the Linear Alkanes of the sample, while still having negligible response to Aromatic or Cyclo-Hydrocarbon components of the sample.

A "PIANO" analysis is a conventional way of characterizing the relative concentrations of different Hydrocarbon groups in Petroleum fuels. In this terminology, "P" is for Paraffins (Linear Alkanes), "I" is for Iso-Paraffins (Branched Alklanes), "A" is for Aromatics, "N" is for Naphthenes (Cyclo-Hydrocarbons), and "O" is for Olefins (Alkenes). Using this terminology, then CCID at low Oxygen concentrations can provide a "P" type of analysis, and at higher Oxygen concentrations a "PIO" type of analysis of Petroleum samples.

Figure 6. 1.0µL injected; 30m x 0.53mm x 1.5µm DB-1ms, He=6 35 -51ºC at 3ºC/min, 51-200ºC at 12ºC/min.

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CCID - VALERO PREMIUM GASOLINE

AUTO DIESEL #2 FUEL

Figure 8. FID vs. CCID comparison for an Auto Diesel sample.

Figure 7. Same gasoline sample as Figure 6. At low Oxygen concentrations, CCID detects Linear Alkanes. As Oxygen increases. More peaks appear due to Alkenes and Branched Hydrocarbons.

Figures 8 and 9 show additional comparisons of CCID versus FID responses for Diesel Fuel and Shale Oil samples, respectively. As with the gasoline samples, CCID at low detector Oxygen concentrations provided peaks mainly due to Linear Alkanes. As the Oxygen concentration is increased in the detector gases, additional peaks appeared in the chromatograms, and these were likely due to Alkene and Branched Hydrocarbon compounds, and were not likely to be Aromatic or Cyclo-Hydrocarbons. These data illustrate how mixtures of Air, Oxygen, and/or Nitrogen supplied through the detector gas lines can be used to produce various selective CCID fingerprint chromatograms for otherwise very complex samples.

Figure 9. FID vs. CCID comparison for a Shale Oil sample.

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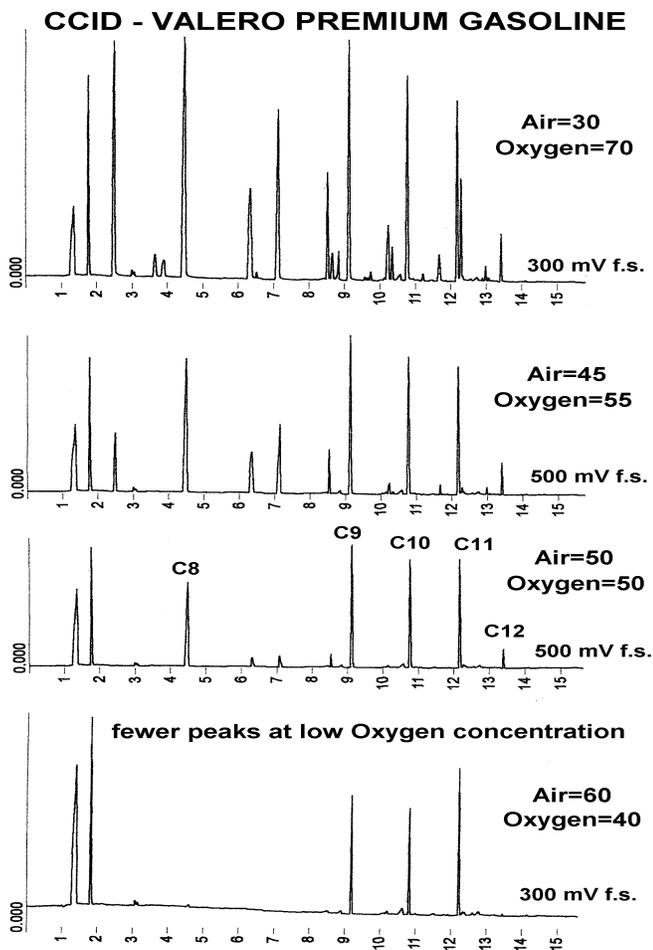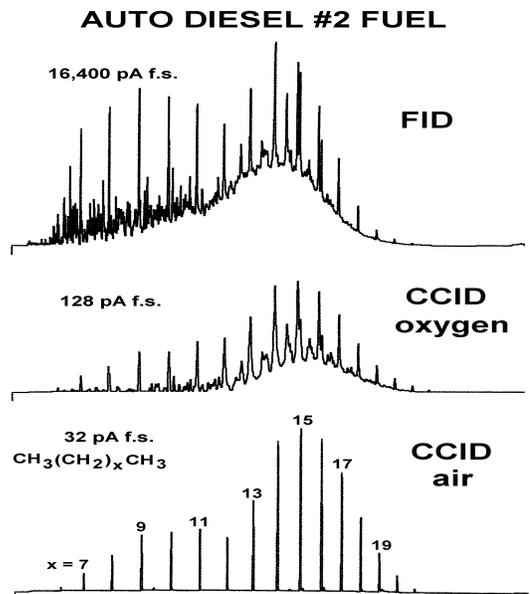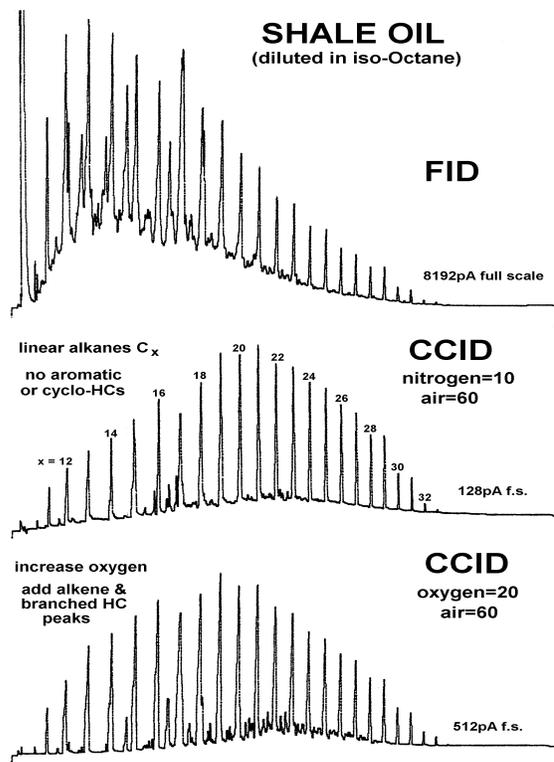www.det-gc.com   e-mail: detplp@aol.com

4.) FAME AND TRIGLYCERIDE RESPONSES VS. DETECTOR OXYGEN

Like Alkanes and Alkenes, FAMEs and Triglycerides are also characterized by chains of CH_2 functional groups. In addition, these two classes of chemical compounds also contain Oxygen heteroatoms which are amenable to selective detection via a Thermionic Surface Ionization process (TID) which uses the TID-10 or TID-1 type ceramic ion source. TID detection in general applies to compounds containing electronegative atoms or functional groups and it involves the direct impact of the sample compound with the surface of the ion source, and the extraction of electrons from that surface to form gas phase negative ions. When the ionizing surface is a TID-10 or TID-1 ceramic, then the process includes selective detection for many Oxygenates, some Halogenates and Nitro compounds, Thiol compounds, and Nitrogen compounds containing the Pyrrole functional group versus the Pyridine group. Unlike CCID detection which is applicable to relatively high sample concentrations, TID-10 or TID-1 detection can provide trace detection and exceptional selectivity for certain types of compounds. In the gasoline data shown earlier in Figure 2, the Ethanol peak in the top chromatogram was due to a TID process, while the Linear Alkane peaks were due to the CCID process.

Figure 10 shows the response of a TID-10 ion source to a mixture of FAME compounds for various combinations of the detector gas environment. The FAMEs included 3 compounds with saturated Carbon bonds (peaks 1, 2, 4) and 1 compound containing a Carbon double bond (peak 3). When the detector gas environment was Nitrogen, the TID surface ionization mechanism prevailed and the relative heights of the saturate to unsaturate sample peaks qualitatively reflected their relative concentrations in the sample. As Oxygen was added to the detector gas, the CCID detection process prevailed and the saturates response dominated that of the unsaturate compound, with the magnitude of difference decreasing with increasing Oxygen concentration.

In Figure 11, the Triglyceride sample analyzed contained 5 compounds with saturated Carbon bonds. In the CCID chromatogram with an Oxygen detector environment, the increasing heights of peaks 1 - 5 reflected the increasing numbers of CH_2 functional groups in the different compounds. In the TID chromatogram with a Nitrogen detector environment, the relative peak heights were similar to that of the FID chromatogram and reflected the selective detection of the glyceryl functionality present in each compound.
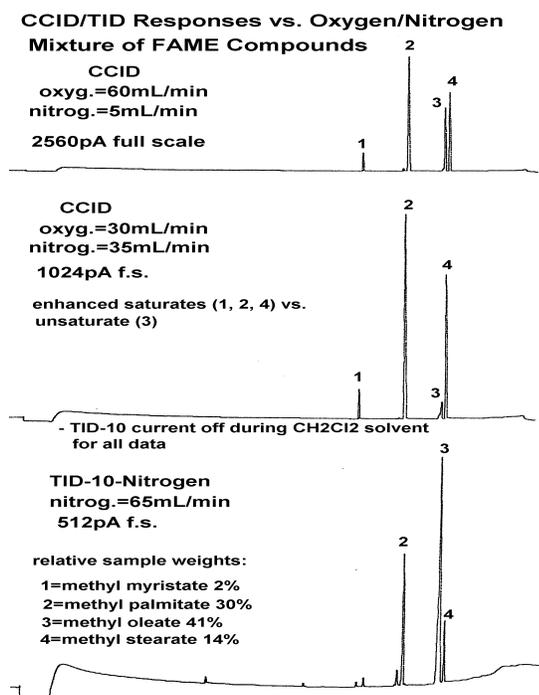
The data presented in this report illustrate the special characteristics of TID-10 and TID-1 ceramics, and the versatility of using the same equipment to achieve a variety of unprecedented chemical detection selectivities.

CCID/TID Responses vs. Oxygen/Nitrogen Mixture of FAME Compounds

CCID
oxyg.=60mL/min
nitrog.=5mL/min

2560pA full scale

CCID
oxyg.=30mL/min
nitrog.=35mL/min

1024pA f.s.

enhanced saturates (1, 2, 4) vs. unsaturate (3)

- TID-10 current off during CH2Cl2 solvent for all data

TID-10-Nitrogen
nitrog.=65mL/min
512pA f.s.

relative sample weights:

1=methyl myristate 2%
2=methyl palmitate 30%
3=methyl oleate 41%
4=methyl stearate 14%

Figure 10. Thermo Trace Ultra GC & DET hardware & Thermo NPD electronics.

TRIGLYCERIDES

FID

5500pA full scale

2000ng each in methylene chloride

1=glyceryl tridecanoate
2=glyceryl tridodecanoate
3=glyceryl trimyristate
4=glyceryl trioctanoate
5=tripalmitin

CCID
(TID-1-Oxygen)

selective for methylene groups

1024pA f.s.

----- peak height increases with number of methylene groups

TID
(TID-1-Nitrogen)

selective for oxygenates

256pA f.s.

----- largely due to TID response to glyceryl group
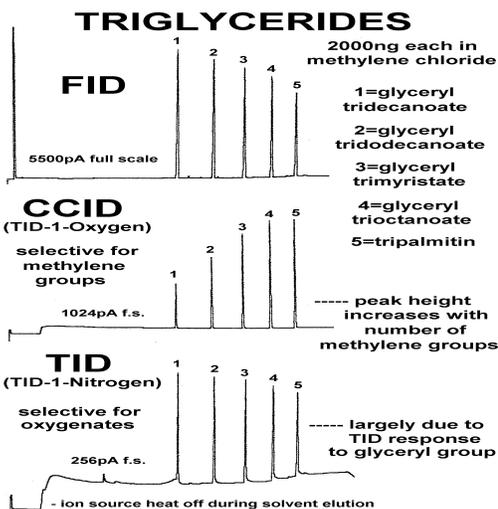
- ion source heat off during solvent elution

Figure 11. Agilent 6890 GC & stand-alone DET Current Supply.