

DET REPORT

NO.68 SUMMER 2014

DETECTOR Engineering & Technology, inc.
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- 1.) CATALYTIC COMBUSTION IONIZATION DETECTION (CCID) - MORE CHARACTERISTICS OF THE SELECTIVITY FOR n-PARAFFINS.
- 2.) FINGERPRINT CHROMATOGRAMS OF GASOLINES BY SELECTIVELY DETECTING ALKANE AND OXYGENATE CONSTITUENTS.
- 3.) GC/CCID - A UNIQUE TOOL FOR INVESTIGATING CATALYTICALLY INDUCED COMBUSTION OF INDIVIDUAL HYDROCARBON AND FAME CONSTITUENTS IN COMPLEX PETROLEUM AND BIOFUEL SAMPLES.
- 4.) INEXPENSIVE EXTENSION OF AGILENT NPD EQUIPMENT TO TID-10 & CCID MODES OF SELECTIVE DETECTION (OXYGENATES, CH₂ GROUPS, etc.).
- 5.) RECENT DEVELOPMENTS IN NP DETECTION ON BRUKER/VARIAN GCs.

By P.L. Patterson

1.) CATALYTIC COMBUSTION IONIZATION DETECTION (CCID) - MORE CHARACTERISTICS OF THE SELECTIVITY FOR n-PARAFFINS.

In DET Report newsletters of recent years, a selective GC detection process called Catalytic Combustion Ionization (CCID) has been described. In this detector, the sample compound itself provides the fuel for a momentary burst of flame ionization as that compound impacts a heated, catalytically-active ceramic surface located in a detector gas environment containing Oxygen. As described previously, CCID provides selectivity for compounds containing chains of the Methylene (CH₂) functional group. It is a simple and especially effective means of selectively detecting n-Paraffin constituents of complex Petroleum samples.

Figure 1 compares FID and CCID chromatograms for a sample comprised of approximately equal amounts of C₅ through C₁₅ n-Paraffins. The data clearly illustrate the characteristic that CCID response gets bigger and bigger with increasing numbers of CH₂ groups in the sample compound.

The CCID chromatogram in Figure 1 was generated using DET's proprietary TID-10 ceramic ion source in a DET Retrofit Tower structure mounted on a Thermo Trace Ultra GC. Thermo's NPD electronics were used to heat the ion source with a precision controlled supply of 2.450 A of electrical current, and polarize the ion source at -90V relative to a surrounding collector electrode. For CCID detection, a TID-10 ion source surface temperature in the range of 300 - 400°C was sufficient to ignite combustion of the n-Paraffin compounds.

Mixture of n-Paraffins (Linear Chain Alkanes)
equal amounts of each C_x compound

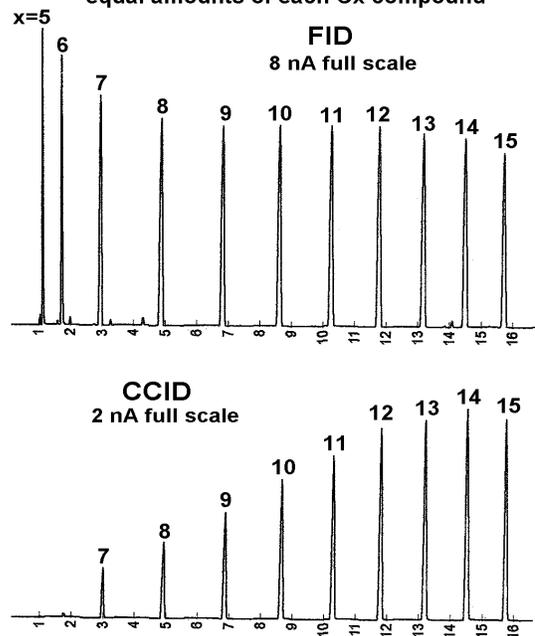


Figure 1. FID vs. CCID chromatograms for n-Paraffins. TID-10 ion source heat = 2.45A, polarization = - 90 V. CCID gases: Air = 30, Oxygen makeup = 50 mL/min. DET retrofit detector on Thermo Trace Ultra GC.

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Effect of changing Oxygen concentration. Figure 2 illustrates how the concentration of Oxygen in the detector gases can affect the relative magnitudes of CCID responses to compounds in the n-Paraffin mix. The higher Oxygen concentration added a C₇ peak and provided a little more uniform responses for C₁₂ - C₁₅. CCID detection requires a sufficient number of CH₂ groups to fuel the momentary burst of flame ionization, so there is a threshold in CH₂ concentration below which the response drops off sharply. For the C₁₅ paraffin, that response threshold corresponds to a compound amount typically in the range of 50 - 200 ng. This response threshold occurs at lower and lower compound amounts with increasing Oxygen concentration, ion source temperature, and number of CH₂ groups.

Effect of changing ion source heating current.

The TID-10 ceramic ion source used in the CCID mode has a wire core, such that the ion source surface temperature is changed by changing the magnitude of electrical current flowing through the core. Figure 3 compares CCID responses at different heating currents. The higher heating current resulted in more than a tenfold increase in response for the C₇ - C₁₅ components of the sample.

CCID Detection of n-Paraffin Mix
equal amounts of C5 - C15 compounds

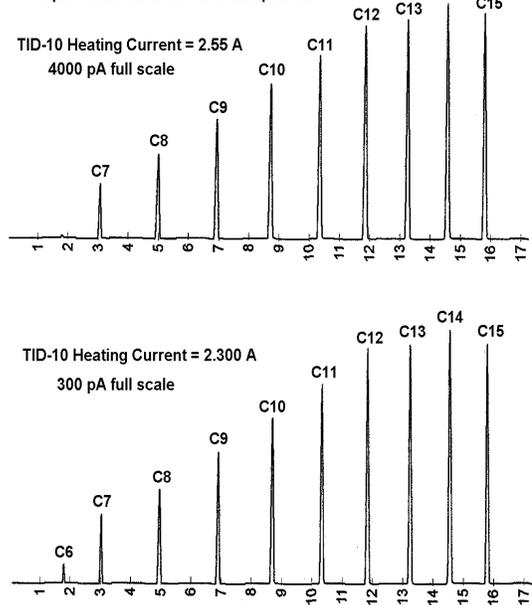


Figure 3. Air=30, Oxygen makeup=50, polarization= - 90 V.

CCID Detection of n-Paraffin Mix
equal amounts of C5 - C15 compounds

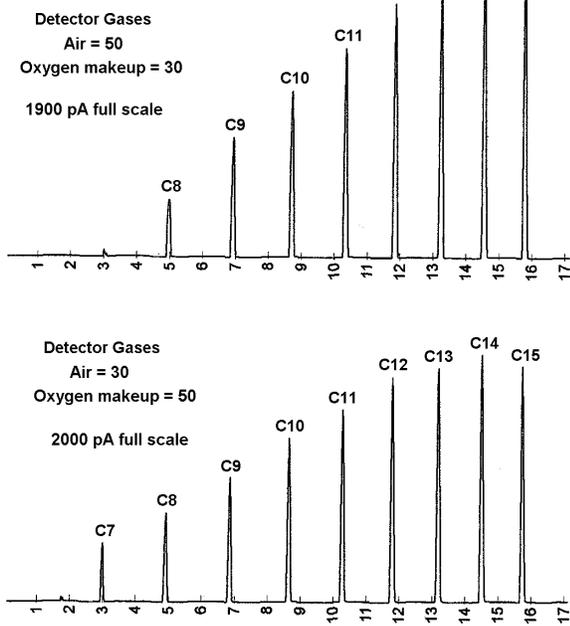


Figure 2. TID-10 heat = 2.450 A, polarization = - 90 V.

CCID Detection of n-Paraffin Mix
equal amounts of C5 - C15 compounds

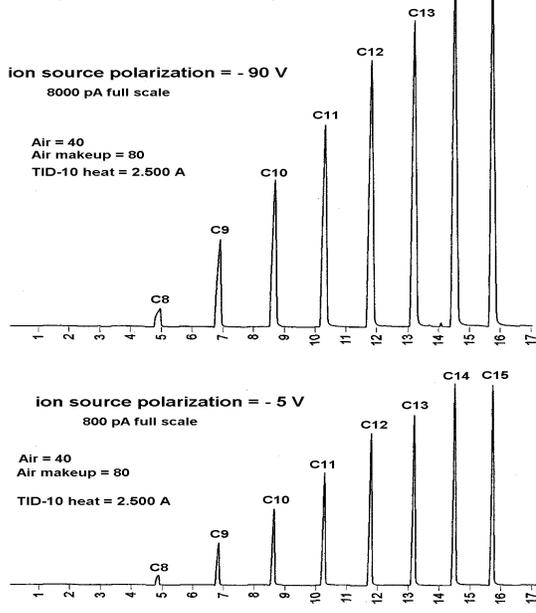


Figure 4. n-Paraffin response at different polarizations.

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Effect of changing Ion Source to Collector Polarization. CCID detection is achieved by modification of NPD equipment. Collection of the ions formed in the momentary burst of a CCID flame occurs best with a polarization voltage of about 50 V or higher between the TID-10 ion source and the ion collector. However many brand NPDs have available only a low polarization of 4 to 5 V which is optimum for NP detection. Figure 4 compares CCID n-Paraffin response at 2 different polarizations. As expected, the higher polarization produced much larger signal magnitudes, although the pattern of relative signals of the different sample components remained unchanged. Among the different brands of available NPD equipment, Thermo Trace GC models are the only ones which have NPD electronics capable of providing both low and high polarizations for optimum operation in any NPD, TID, or CCID mode of operation. For some other brand NPDs, DET has available a stand-alone Current Supply module that can also provide both low and high polarizations.

One other feature to be noted of the Figure 4 data is that they were generated using a high flow of Air as the detector makeup gas versus the Oxygen makeup used in earlier data.

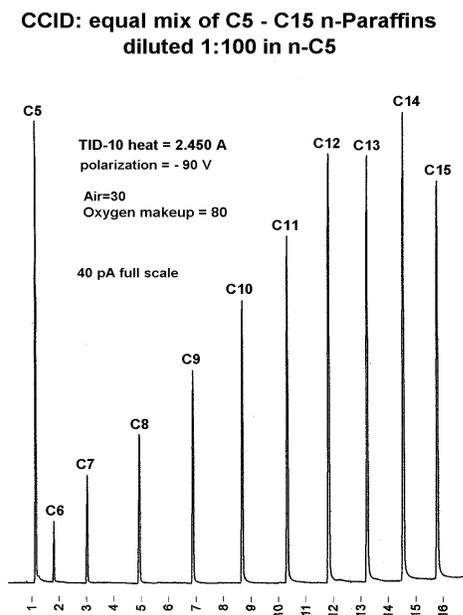


Figure 5. n-Paraffins diluted in n-C₅.

Dilution of the n-Paraffin sample. Figure 5 shows a CCID chromatogram of the C₅ - C₁₅ Paraffin sample diluted 1 part to 100 in n-C₅. A high Oxygen makeup gas flow was used for these data so that all the compounds exceeded the concentration threshold for onset of CCID detection.

n-Paraffins versus iso-Paraffins. Figure 6 compares FID and CCID chromatograms for a sample in which 2 iso-Paraffins (2-Methylheptane and 4-Methyloctane) were added to the earlier n-Paraffin mix. Whereas the FID gave comparable peak heights for the iso-Paraffins and adjacent n-Paraffins, CCID peak responses for the iso-Paraffins were substantially smaller than their linear chain counterparts. Furthermore, by additional reduction in the concentration of Oxygen in the detector, the iso-Paraffins were effectively removed from the chromatogram. This difference between linear and branched Paraffin compounds, and the dependence on detector Oxygen has also been described in earlier DET Reports. There is a similar difference between n-Paraffins and Olefins.

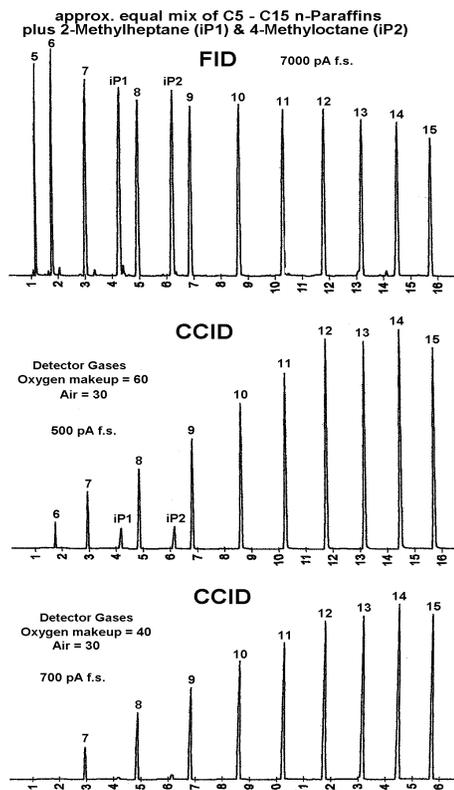


Figure 6. CCID data: TID-10 heat = 2.450 A, polarization = -90 V

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2) FINGERPRINT CHROMATOGRAMS OF GASOLINES BY SELECTIVELY DETECTING ALKANE AND OXYGENATE CONSTITUENTS.

A TID-10 ion source, and its predecessor TID-1 ion source, have been used to illustrate the unique selectivity of CCID detection. In addition to the Catalytic Combustion Ionization process, both of these ion sources also produce selective responses for certain types of Heteroatom compounds by means of a direct Thermionic Surface Ionization (TID-10) process. Oxygenates, Halogenates, Thiols, and compounds containing Nitro or Pyrrole groups are examples of responders to TID-10 surface ionization, whereas CCID responds mainly to high concentrations of Hydrocarbons and FAMES that contain chains of Methylene groups. Hence, when a CCID detector is applied to a real world Petroleum sample, the resulting chromatogram can contain peaks corresponding to both CCID and direct TID-10 ionization.

Figure 7 compares FID and CCID chromatograms of a gasoline sample obtained from a local station in Walnut Creek, CA. The FID chromatogram clearly demonstrates the complex nature of the sample, while the CCID chromatogram demonstrates the easy identification of peaks associated with Linear Alkane constituents of that sample. In addition, the CCID chromatogram includes a couple of small peaks associated with iso-Alkane constituents, as well as peaks corresponding to Alcohol constituents as detected by a direct TID-10 process.

Figure 8 compares CCID chromatograms of 2 different brands of Gasoline. These unique simplified data illustrate different peak fingerprint patterns for the 2 samples that would otherwise not be obvious by using only a comparison of FID chromatograms.

GASOLINE ANALYSIS

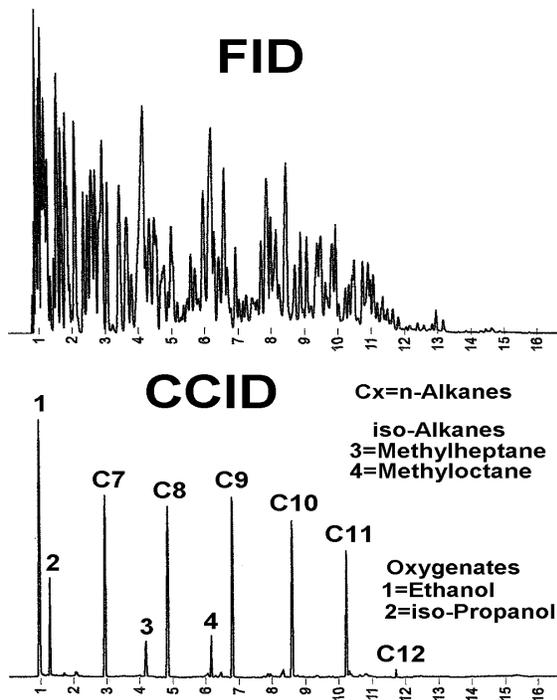


Figure 7. 0.5 μ L direct injection, Valero gasoline. Thermo Trace Ultra GC with DET retrofit FID/CCID detector hardware & Thermo NPD electronics. 30m x 0.53mm DB1, He=8, 40-60 $^{\circ}$ C at 5 $^{\circ}$ C/min, 60-190 $^{\circ}$ C at 10 $^{\circ}$ C/min. CCID Air=30, Oxygen makeup=50, TID-10 heat=2.450A, polarization= - 90V, detector T=250 $^{\circ}$ C, Injector=190 $^{\circ}$ C.

CCID ANALYSIS OF GASOLINES

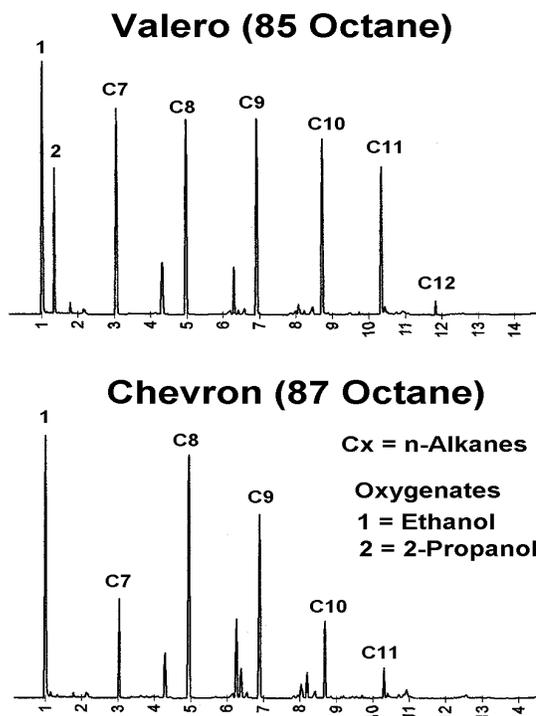


Figure 8. Gasoline samples from local stations in Walnut Creek, CA. Same conditions as Figure 7.

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Figure 9 shows the Chevron data of Figure 8 at an amplified signal display to illustrate other components detected in the sample. These are likely due to more Branched Hydrocarbon or possibly Alkene constituents of the Gasoline. Previous DET Reports have shown that additional selected peaks can be added or removed from the displayed Gasoline fingerprint through judicious adjustments of the Oxygen concentration in the detector gases. Figure 10 illustrates this further for the Valero sample described earlier.

As mentioned earlier, existing NPD electronics on some GC brands are restricted to low polarization voltages for the ion source. Figure 11 compares analyses of the Valero Gasoline sample at low and high values of ion source polarization. The major difference in the 2 chromatograms is just the absolute magnitude of the peak signals. Whereas the top chromatogram in Figure 11 was generated with Thermo Trace Ultra NPD electronics, the bottom chromatogram would be representative of an analysis generated using existing Agilent NPD electronics to power the TID-10 ion source.

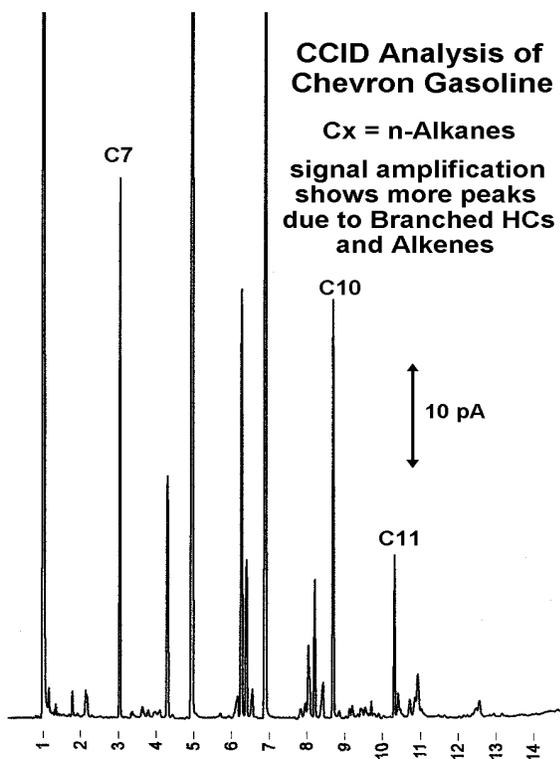


Figure 9. Amplified Chevron Gasoline chromatogram.

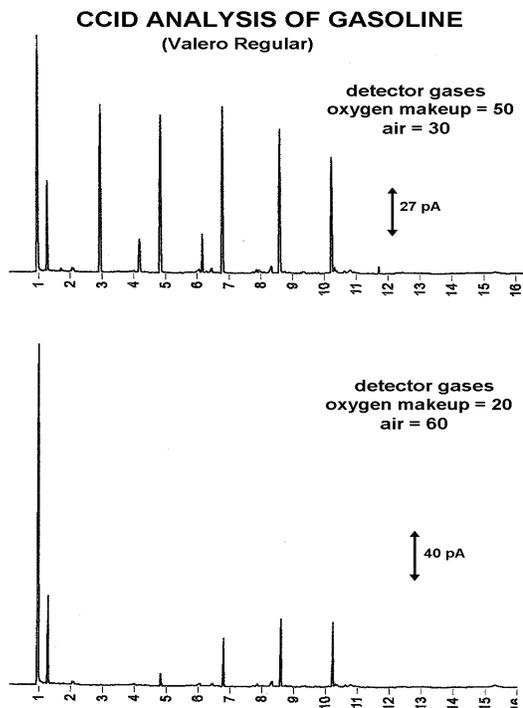


Figure 10. Valero Gasoline CCID fingerprint at different Oxygen concentrations.

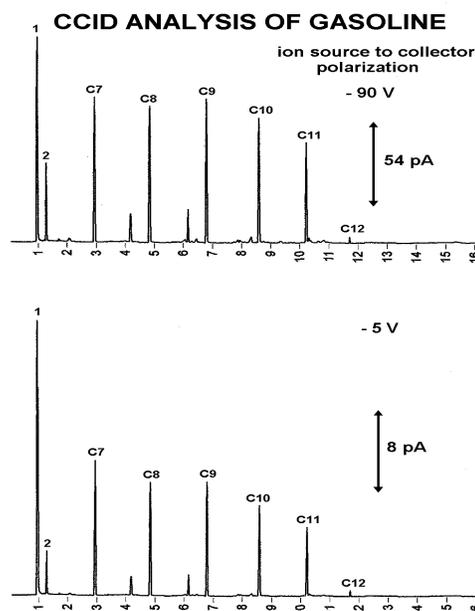


Figure 11. Valero Gasoline fingerprint at different polarizations.

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3.) GC/CCID - A UNIQUE TOOL FOR INVESTIGATING CATALYTICALLY INDUCED COMBUSTION OF INDIVIDUAL HYDROCARBON AND FAME CONSTITUENTS IN COMPLEX PETROLEUM AND BIOFUEL SAMPLES.

Improved combustion of Petroleum and Biofuels is a subject of continuing high interest. The combination of GC separation and CCID detection provides a unique tool for further understanding how individual constituents in these fuels contribute to the combustion process.

Equipment used in CCID detection is illustrated in Figure 12. It involves a 1/16 inch diameter ceramic ion source element molded over a wire core to provide a means of electrically heating the element over a wide temperature range. The ion source is located in a flowing gas stream comprised of effluent from a GC column and detector gases which contain various levels of Oxygen. As an appropriate sample compound elutes from the GC, it ignites a momentary flame upon impact with the heated ceramic, and the resulting burst of ionization forms the detection signal measured at a surrounding electrode.

To date, the most interesting CCID detection has involved a catalytically active TID-10 ceramic or its predecessor TID-1 ceramic. DET's method of forming ion sources is amenable to creating an almost unlimited number of other ceramic formulations that can also be investigated for different characteristics with respect to catalyzing combustion ignition of compounds.

An important characteristic of the TID-10 (and former TID-1) ceramic is that it has a relatively low work function for the emission of electrical charge, and that appears to be a contributing factor to being able to catalyze combustion ignition of certain Hydrocarbon compounds at a relatively low temperature of 300-400°C.

CCID detection with a TID-10 ion source has already revealed interesting differences between the catalytic combustion ignition of different classes of Hydrocarbon molecules. As mentioned earlier, CCID is especially applicable to detection of compounds like Linear Alkanes or Saturated FAMES which contain chains of Methylene (CH₂) functional groups. At the same time, there are negligible responses for Aromatic or Cyclo-Hydrocarbons as illustrated in Figures 13 and 14.

Figures 15 and 16 illustrate further differences between CCID detection of Linear vs. Branched Alkanes, as well as differences between Alkanes and Alkenes, and how those differences are affected by the concentration of Oxygen in the detector gases.

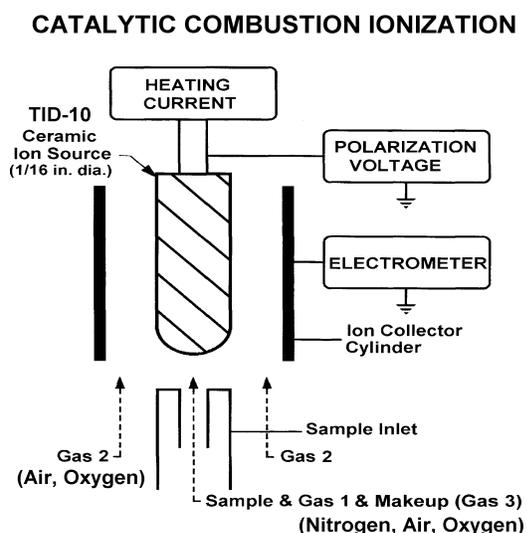


Figure 12.

TID & CCID DISCRIMINATION VS. AROMATIC HC

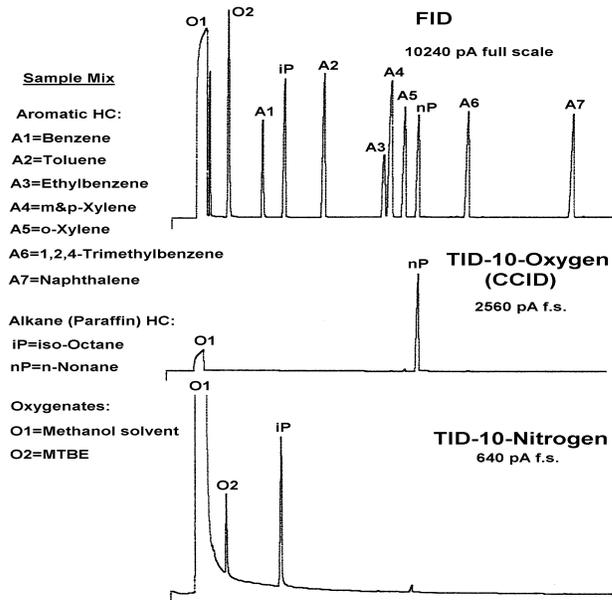


Figure 13. CCID responds to the linear Alkane (n-Nonane) but not to the Aromatic ("A" labels), iso-Octane, or MTBE components.

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CCID observations to date have raised many interesting questions which relate to the fundamental chemistry of combustion. Some examples are as follows:

1. What is the special catalytic property of a TID-10 ceramic that provides for low temperature combustion ignition of compounds containing chains of CH₂ while at the same time not igniting Aromatic or Cyclo-Hydrocarbons? Are there other catalytic ceramic formulas that selectively ignite the Aromatics?
2. For compounds that contain chains of many CH₂ groups, why does the presence of a branched Methyl (CH₃) group, or a Carbon double or triple bond result in suppression of the combustion ignition unless the Oxygen concentration is substantially increased?
3. Is there a further difference in combustion ignition depending on the number of branched Methyl groups, or on the molecular position of a Carbon double bond or branched Methyl group?

GC/CCID equipment provides a tool that is well suited for further investigations of these types of fundamental chemical issues. The GC introduces well defined compounds into the detector; the ion source configuration allows many different catalytic ceramics and temperatures to be studied; and 2 or 3 detector gas lines allow different gas environment combinations.

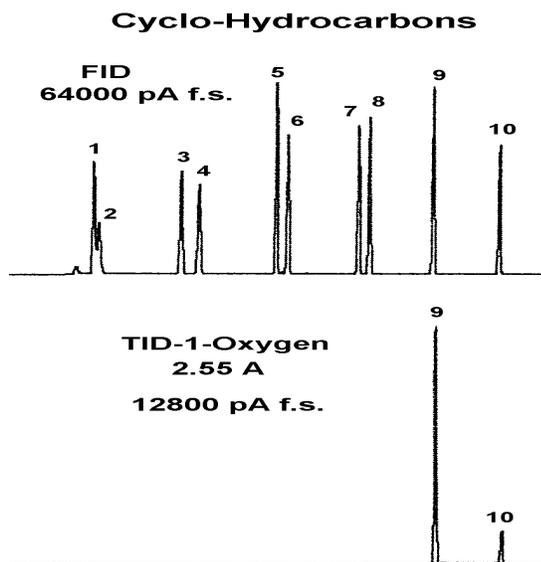


Figure 14. CCID (TID-1-Oxygen) detection: equal volumes, 1=Cyclopentene, 2=Cyclopentane, 3=Cyclohexane, 4=iso-Octane, 5=Toluene, 6=Cycloheptane, 7=Cycloheptene, 8=Cyclooctane, 9=Dicyclopentadiene, 10=n-Dodecane.

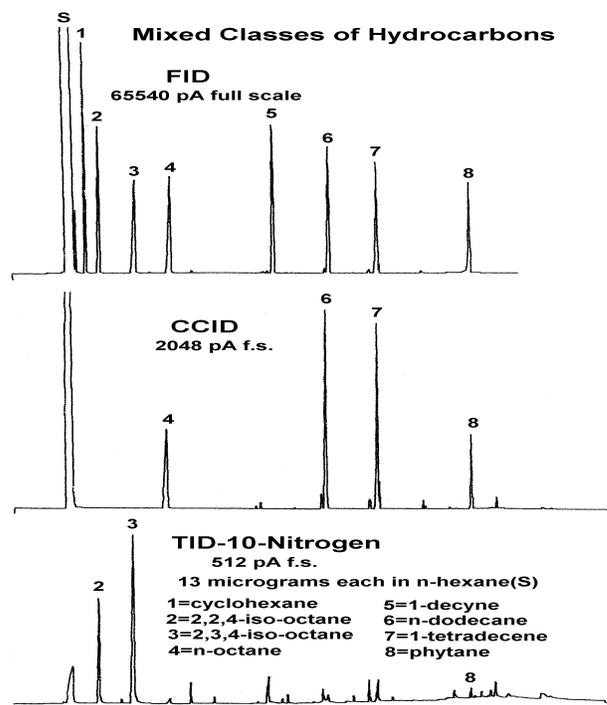


Figure 15. Sample containing different Hydrocarbon classes
CCID: O₂ through "Air" line = 60, N₂ makeup = 5 mL/min.

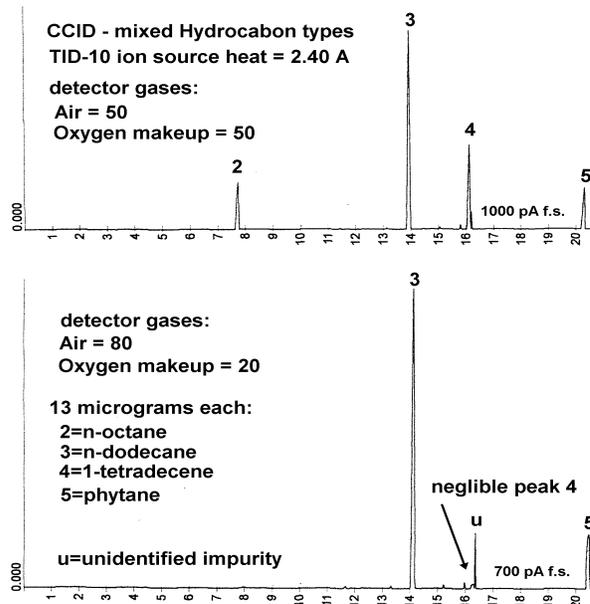


Figure 16. Effect of varying Oxygen concentration on relative response to different Hydrocarbon compounds.

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4.) INEXPENSIVE EXTENSION OF AGILENT NPD EQUIPMENT TO TID-10 & CCID MODES OF SELECTIVE DETECTION (OXYGENATES, CH₂ GROUPS, etc.).

Agilent designed the NPD equipment on the 6890 GC to be compatible with the standard hexagonal flanged ion sources manufactured by DET, and the 7890 NPD is the same. Therefore, any available DET ceramic ion source can be directly installed into these Agilent instruments.

Figure 17 illustrates the configuration of a 6890/7890 NPD. For users of this equipment, DET offers two suggestions for achieving optimum performance even in the NP mode. One suggestion is to not use Agilent's Adjust Offset method of setting the Bead Voltage to heat the ion source. That procedure inevitably leads to operating the ion source hotter than it needs to be, and that reduces the ion source's operating life. Furthermore, Adjust Offset is not relevant to TID-10 or CCID detection. The second suggestion is to replace the small orifice NPD jet with a wide bore jet so that capillary columns can be inserted clear through the jet to a termination close to the bottom of the ion source. This eliminates any sample degradation due to contact with the internal metal of the jet. A wide bore jet/column positioning tool kit is available from DET to facilitate this column installation.

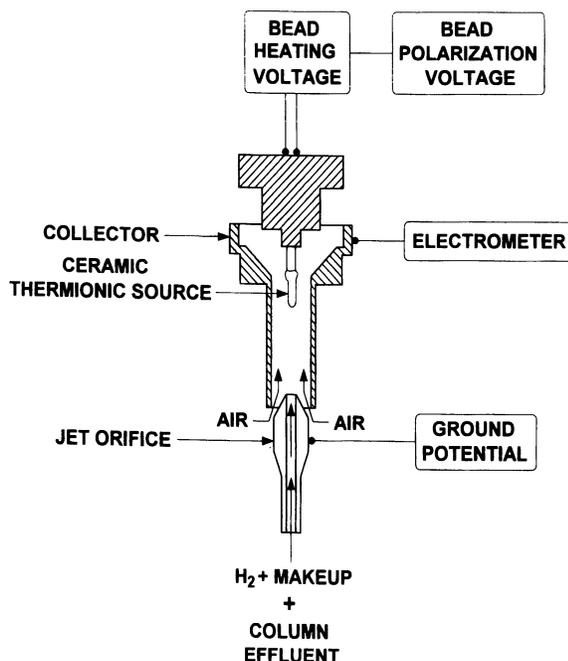


Figure 17. Schematic illustration of an Agilent NPD.

Converting an Agilent NPD to TID-10 or CCID detection is a simple matter of installing a TID-10 ion source, and supplying Nitrogen, Air, Oxygen, or combinations thereof, through the 3 gas lines that normally supply Hydrogen, Air, and Makeup gases to the detector. However, there is a limiting factor with the existing Agilent NPD electronics in that the Bead Voltage polarizes the ion source at only one fixed value of about - 4.4 Volts, and this does not provide the most optimum ion collection efficiency for the TID-10 and CCID modes.

One means of achieving optimum TID-10/CCID detection with Agilent NPD equipment is to substitute a stand-alone DET Current Supply as the means of powering the ion source. Figure 18 shows that a polarization of -45 V as available from the DET supply produces TID-10/CCID signal magnitudes which are almost 10 times larger than those provided by the Agilent Bead Voltage supply.

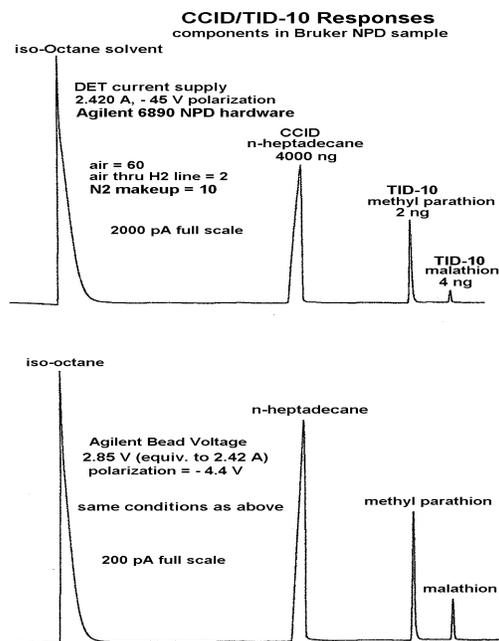


Figure 18. Comparison of TID-10 ion source heated with equivalent power by a DET Current Supply and Agilent Bead Voltage supply. CCID process provides signal for the large concentration of the Hydrocarbon component, while TID-10 surface ionization process detects trace Heteroatom components.

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An earlier DET Report described peak saturation that occurred for high concentration triglycerides when the ion source polarization was not high enough to adequately separate the positive and negative gas phase ions formed in the momentary burst of CCID flame ignition. It was shown that the peak saturation problem was alleviated by replacing the standard Agilent NPD collector with a collector of smaller internal diameter. For the same polarization, a smaller internal diameter produces a bigger electric field between the ion source and collector.

A smaller ID NPD collector can be purchased from Agilent (part # G1534-20660). Alternatively, DET has developed several smaller ID inserts that are easily placed inside the standard Agilent collector. Figure 19 compares chromatograms for collectors with different internal diameters, using the same Agilent Bead Voltage to heat and polarize the ion source. As already mentioned, reducing the collector ID increases the electric field for improved ion collection. Reducing the ID also decreases the ion source surface temperature due to increased heat loss to the surrounding detector structure. This decreased surface temperature is a main reason for the differences in relative signals from the different sample components analyzed in Figure 19.

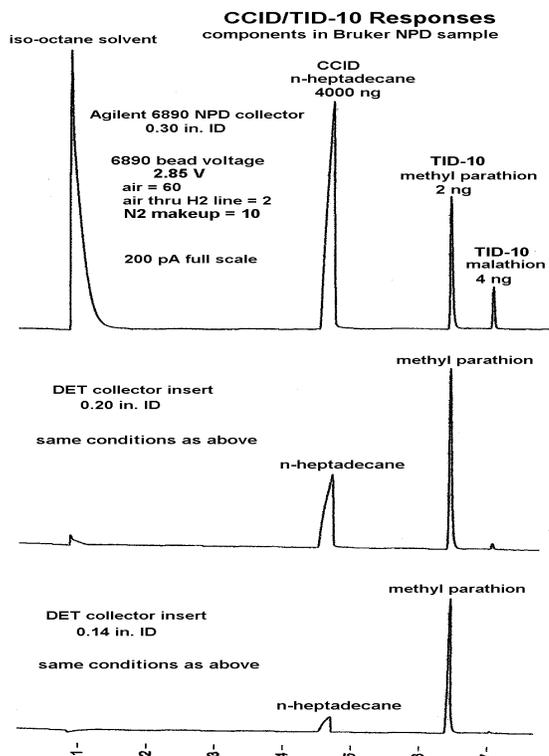


Figure 19. CCID/TID-10 responses for ion collectors of different internal diameters. Same Agilent Bead Voltage for all.

5.) RECENT DEVELOPMENTS IN NP DETECTION ON BRUKER/VARIAN GCs.

Recently, DET entered into collaboration with Bruker to provide ceramic coatings on NPD bead sub-assemblies supplied by Bruker. Bruker's NPD detector structure is unchanged from the TSD structure first introduced by Varian in the late 1970's. The bead is attached to a probe arm that inserts into the side of an NPD tower so as to provide the configuration illustrated in Figure 20. The bead itself is comprised of a helical wire coil core covered over by ceramic material. Compared to other brand NPD ion sources, this bead is relatively large, and that presented challenges in the ceramic coating.

One important observation was that the bead does not heat to a uniform temperature, such that the sides of the bead closest to the helical coil were often hotter than the bottom or top center surfaces. That is a concern because it is precisely the bottom center of the bead where incoming samples interact with the bead, and that is the location where there needs to be the most active Hydrogen-Air chemistry to produce the best NP response. Hydrogen-Air chemistry ignited locally at a

VARIAN/BRUKER TSD/NPD

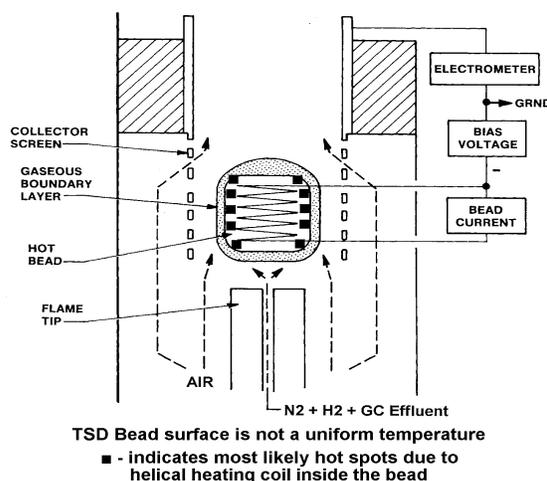


Figure 20. Schematic of a Varian/Bruker TSD/NPD.

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hot spot on the side does not contribute much to the NP response.

In a similar consideration, active ceramic coating on the sides and top of the bead do not contribute much to the NP response. Consequently, DET developed a Hybrid Ceramic coating for the Bruker bead as depicted in Figure 21. With this coating, the sides and top of the bead are covered with an inactive ceramic material, and an active coating is applied only on the bead bottom where samples impact the bead. Compared to earlier coatings for Varian/Bruker beads, the Hybrid coating features less tailing of P peaks, better selectivity versus Hydrocarbons, less heating current required to ignite the NP chemistry, and improved resistance to ceramic cracking and corrosion of the heating coil. Hybrid coated NPD beads are available from Bruker.

Alternative DET Retrofit NPD/TID/CCID/FID Hardware for Installation on a Varian/Bruker TSD/NPD Base.

Instead of the Varian/Bruker TSD/NPD, DET has an alternative detector tower structure that mounts easily onto the Varian/Bruker base. As shown in Figure 22, the DET structure features top mounting of DET's standard hexagonal flanged ion sources. Any DET ion source type can be accommodated so that the same structure can be used to provide NPD, TID, CCID, or FID modes of



Figure 22. Varian/Bruker NPD at top, DET retrofit NPD/TID/CCID/FID equipment at the bottom.



Figure 21. DET hybrid coating for Varian/Bruker NPD bead.

detection. The DET retrofit also includes a ceramic tipped jet that seats into the Varian/Bruker base with a stainless steel ferrule rather than the crushable ferrules used with Varian/Bruker towers. The DET retrofit is compatible with operation using the existing Varian/Bruker TSD electronics, or a stand-alone DET Current Supply can be substituted for powering the ion sources with a higher polarization voltage for optimum response in non-NP modes. Price of a DET retrofit tower is \$1750 and all DET ion sources are \$410 each.



Figure 23. DET retrofit tower mounts onto Varian/Bruker base with 2 short screws, and includes a ceramic tipped jet that seals with a stainless steel ferrule.