

DET REPORT

NO.71 JULY 2016

DETECTOR Engineering & Technology, inc.
486 North Wiget Lane
Walnut Creek, CA 94598-2408 USA
Phone: 925-937-4203; FAX: 925-937-7581
www.det-gc.com e-mail: detplp@aol.com

1.) CATALYTIC COMBUSTION IONIZATION (CCID) & HOT WIRE COMBUSTION IONIZATION (HWCID) DETECTION ADAPTIONS OF NPD EQUIPMENT.

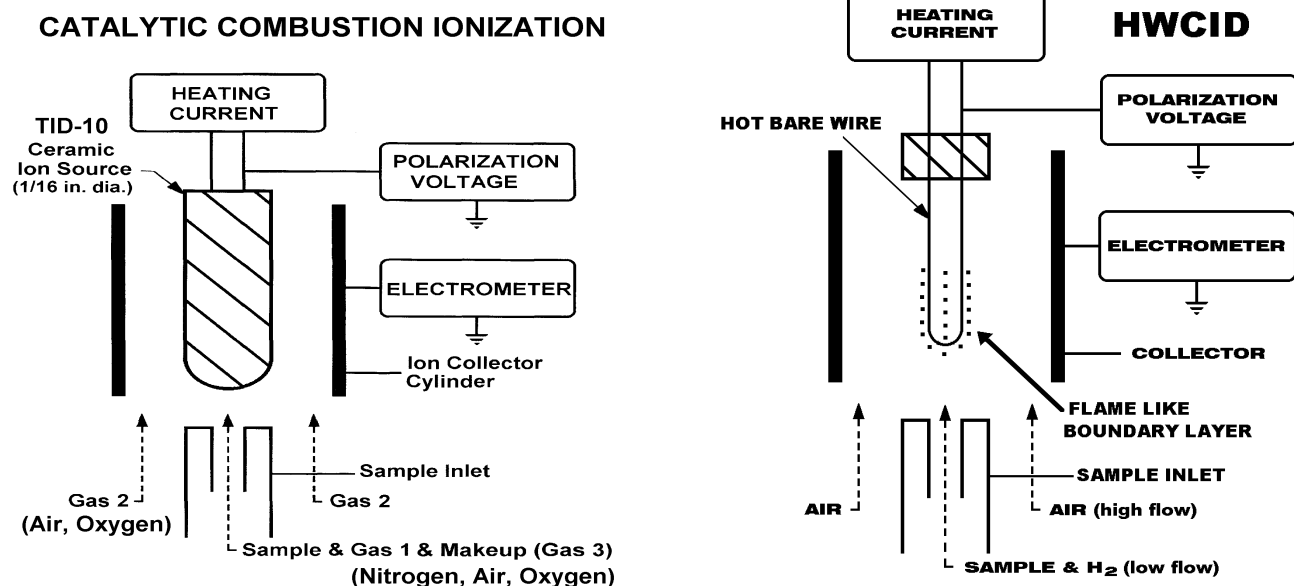
2.) CCID & HWCID ANALYSES OF SELECTED GASOLINE CONSTITUENTS.

1.) CATALYTIC COMBUSTION IONIZATION (CCID) & HOT WIRE COMBUSTION IONIZATION (HWCID) DETECTION ADAPTIONS OF NPD EQUIPMENT.

An NPD is one of the selective detectors commonly supplied by most GC manufacturers. It provides detection of trace level N or P compounds characteristic of applications such as pesticides or drugs of abuse analyses.

Key components of a state of the art NPD are an electrically heated ion source element located on the axis of a concentric cylinder collector electrode, and the required detector gases are a dilute mixture of Hydrogen in Air. NP selective detection occurs when the ion source is heated sufficiently (600 - 800°C) to ignite the Hydrogen and Air in the gaseous boundary layer surrounding the ion source.

One of the founding concepts of DET was development of cylindrical ion sources made of ceramic materials. Another concept was recognition that the NPD operating mechanism was a surface ionization process as opposed to a gas phase ionization process. It then became clear that the basic equipment normally used for NP detection could be inexpensively adapted to other modes of selective detection by simple changes in the type of ion source used and the type of detector gases supplied. The CCID and HWCID modes of detection described in this report are examples of such adaptations of NPD equipment.



CCID detectable compounds are the fuel for momentary bursts of flame ionization as each compound impacts a catalytically active TID-10 ceramic ion source surface. This detection provides **selectivity for compounds containing chains of Methylene (CH₂) groups.**

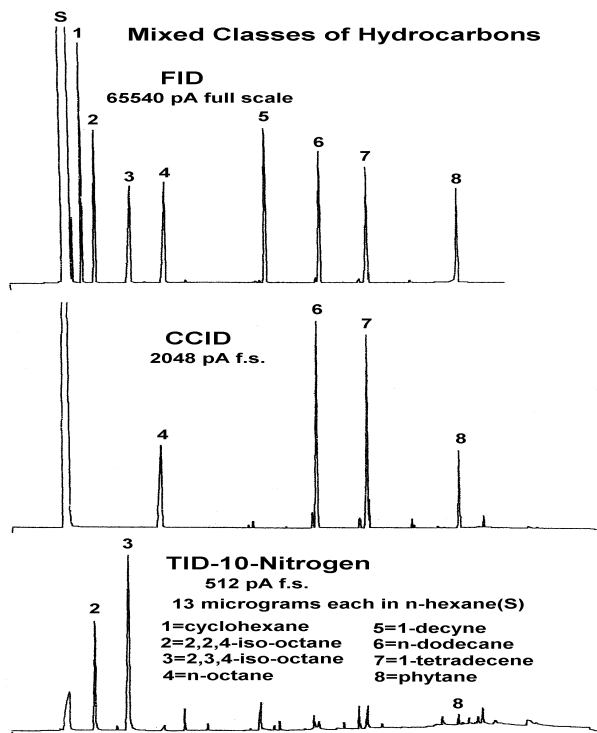
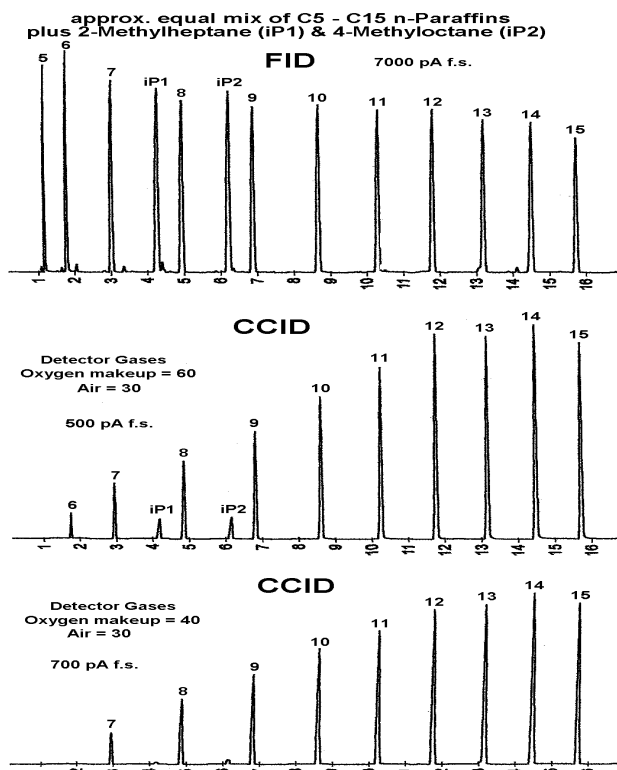
HWCID uses a hot bare wire to ignite a boundary layer of Hydrogen - Air chemistry around the wire. High Air and low Hydrogen flows prevent the ignited chemistry from flashing back to a self-sustained flame. This detection provides **universal responses.**

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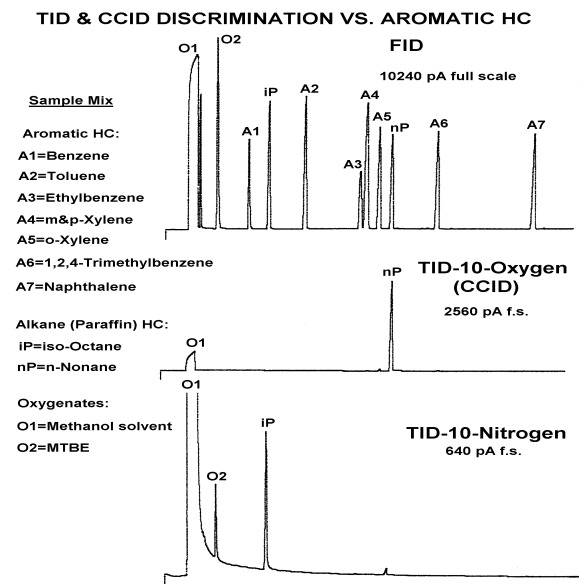
ILLUSTRATIONS OF THE UNIQUE RESPONSE CHARACTERISTICS OF CCID

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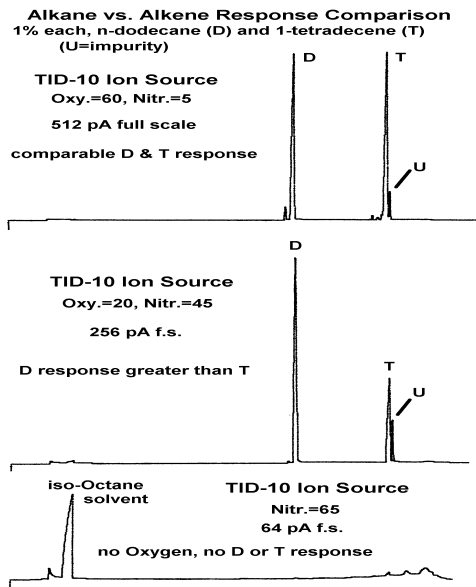


Increasing CCID response with increasing CH₂ groups. Linear HC response greater than Branched HC. Ratio of Linear to Branched decreases with increasing O₂.

No CCID response to Cyclo-HC, iso-Octanes, or triple bonded C compound. Comparable Paraffin to Olefin response at high O₂.



No CCID response to Aromatic HC.



Paraffin to Olefin ratio increases with decreasing O₂.

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2.) CCID & HWCID ANALYSES OF SELECTED GASOLINE CONSTITUENTS

Gasoline formulations differ depending on brand, octane grade, and season of the year. Because of the hundreds of chemical compounds present, identifying differences in gasoline blends can be both time consuming and expensive if GC-FID or GC-MS methods are used. CCID, and to some extent HWCID, are inexpensive selective detection methods that allow differentiation between blends to be accomplished without requiring detailed chromatographic separation of all the gasoline constituents. This is illustrated in Figure 1 which compares FID and CCID chromatograms for a gasoline sample, and in Figure 2 which compares CCID chromatograms for 2 different brands of gasoline. For both of these figures, CCID operating conditions were such that the dominant hydrocarbon response was due to n-Paraffins.

In addition to Hydrocarbon responses, a "CCID" chromatogram often also includes peaks associated with Heteroatom compounds like Oxygenates (e.g., Ethanol in gasoline). These heteroatom responses are due to direct surface ionization on CCID's catalytically active TID-10 ion source. Because it has a relatively low work function, a TID-10 ion source can directly transfer negative charge to compounds like Oxygenates that are electronegative. Unlike CCID which requires Oxygen in the detector gases and involves momentary combustion ignition of the sample compound, this TID-10 surface ionization process does not involve sample combustion and is active in both inert and oxidizing detector gas environments.

GASOLINE ANALYSIS

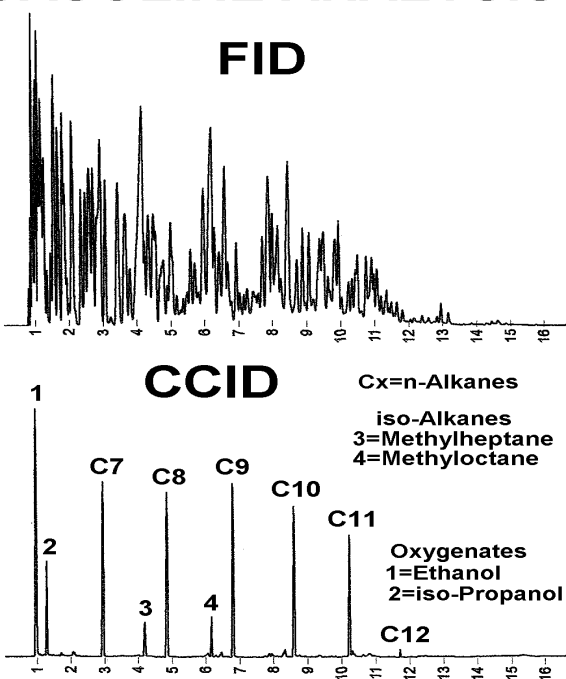


Figure 1. FID vs. CCID with a DET retrofit detector mounted on Thermo Ultra GC & powered by Thermo NPD electronics. 0.5µL Gasoline, 30m x 0.53mm x 1.5µm DB1, He=8, 40-60°C at 5°C/min, 60-190°C at 10°C/min, detector=250°C. CCID conditions: Air=30, O₂ makeup=50mL/min, TID-10 ion source heat=2.45A, polarization= - 90V.

CCID ANALYSIS OF GASOLINES

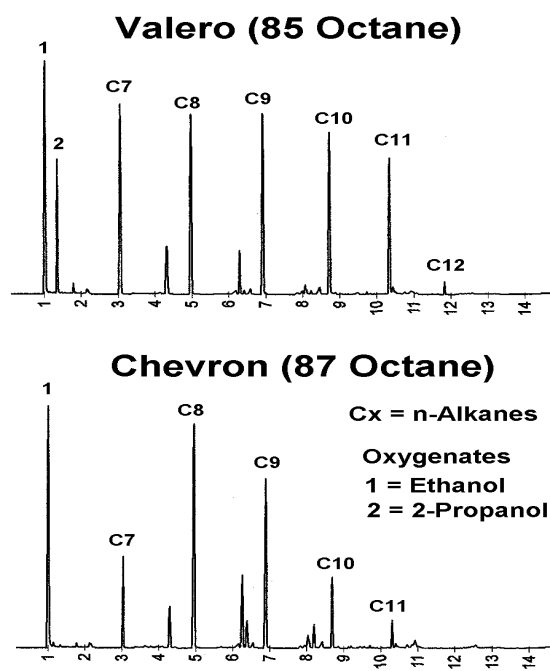


Figure 2. CCID analysis comparison of 2 different brands of gasoline. Same conditions as Figure 1. Difference in Paraffin & Oxygenate peak fingerprints would be difficult to ascertain if comparing only FID chromatograms such as in Figure 1.

CCID responses require sufficient numbers of CH₂ groups to fuel the momentary burst of flame ionization as the sample compound impacts the catalytically active TID-10 surface. That means that CCID responding compounds have a threshold level of sample amount below which the response drops off sharply. For a compound like n-C₁₆, that threshold is in the range of 100 - 200 ng. Compounds with more CH₂ groups have a threshold at a lower ng level, while compounds with fewer CH₂ groups have a threshold at a higher ng level. Also, the threshold for any given compound will occur at a lower ng level for higher concentrations of O₂ in the detector gas, and for higher TID-10 surface temperatures.

Figure 3 shows Gasoline CCID responses at different levels of O₂ in the detector gas. At the lowest O₂, only n-Paraffins with the most CH₂ groups exceeded the CCID response threshold. As O₂ was increased further, additional n-Paraffin peaks appeared, followed by increasing peaks due to iso-Paraffins and Olefins.

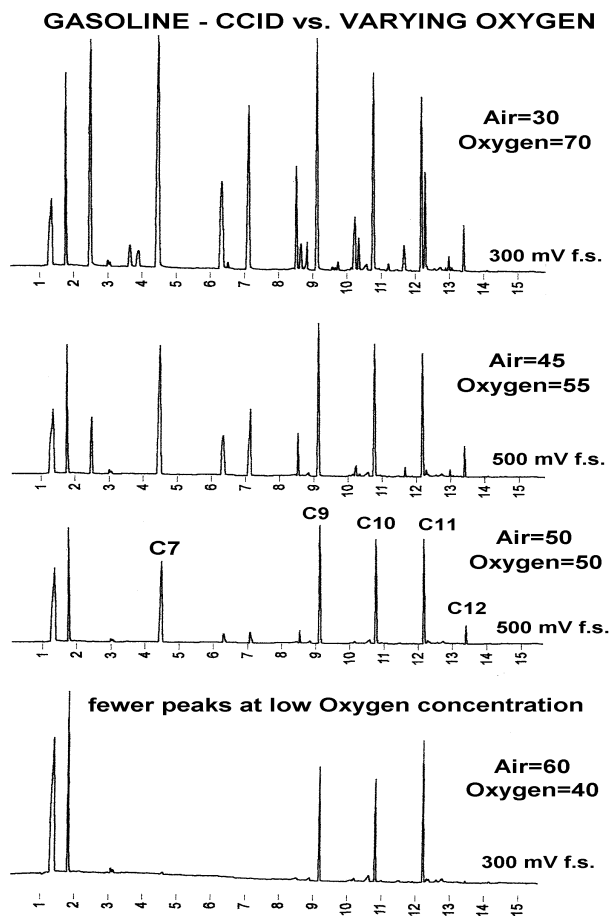


Figure 3

Figure 4 shows a comparison of FID, HWCID, and CCID chromatograms of another Gasoline sample. The O₂ concentration for the CCID data was chosen to be high enough to reveal some iso-Paraffins as well as Olefin constituents in the gasoline along with the n-Paraffins. These additional peaks provide a more detailed CCID fingerprint basis for comparing different gasoline samples.

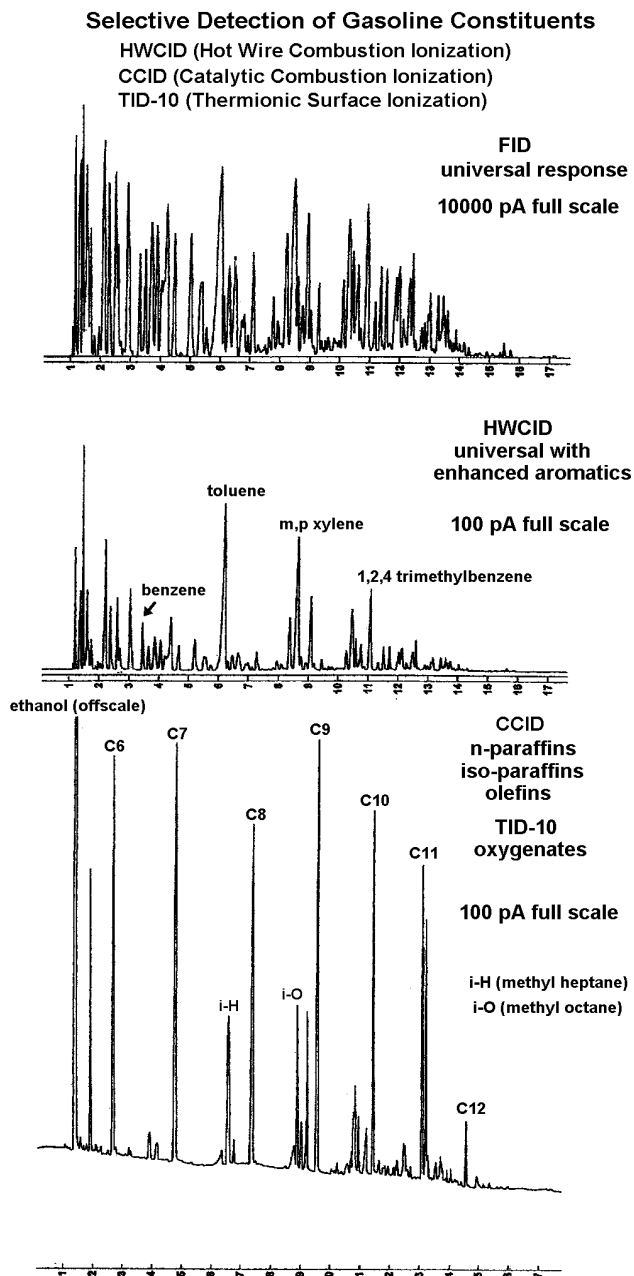


Figure 4

The FID, HWCID, and CCID data in Figure 4 were all generated with DET retrofit equipment mounted on a Thermo Trace Ultra GC as in Figure 1. The CCID data used a TID-10 ceramic ion source element, while the FID and HWCID data substituted a bare wire ignitor/polarizer probe in place of the TID-10 ion source. For the FID, the bare wire was heated sufficiently to ignite a mix of $H_2 = 35$ - Air = 300 mL/min, so that a self sustained flame was created at a ceramic tipped jet. After FID flame ignition, heating current to the bare wire was reduced to 1.0 A. For the HWCID, the bare wire was continuously heated with 3.20 A to ignite a mix of $H_2 = 5$ - Air = 250 mL/min in a flame-like boundary layer that remained near the hot wire. The HWCID provided universal response to all the gasoline constituents, but with enhanced responses to Aromatic HCs as seen in Figure 4. HWCID responses were about 100 times smaller than the FID responses.

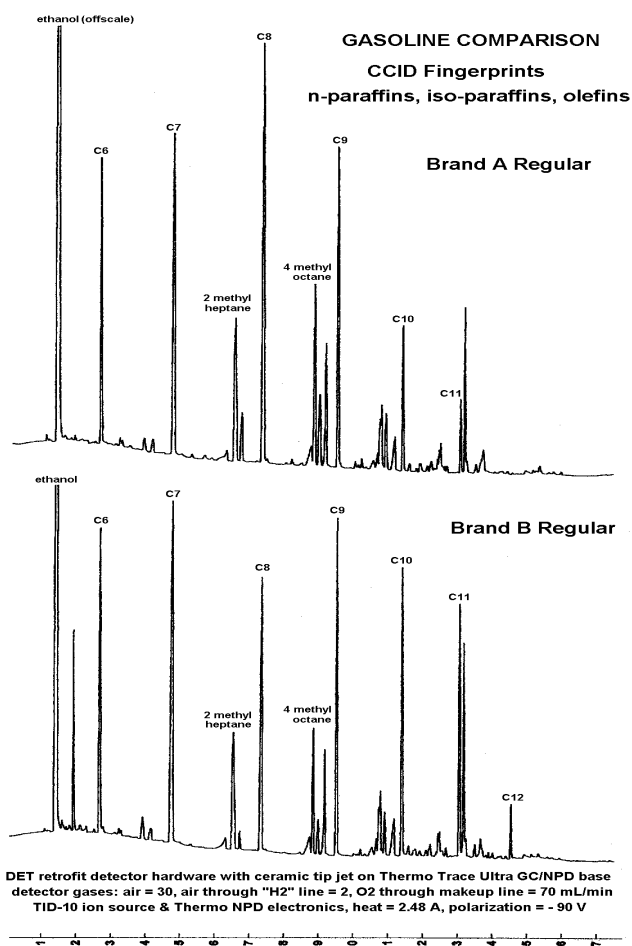


Figure 5.

Figure 5 compares CCID chromatograms for the same two brands of gasoline analyzed in Figure 2. These data were obtained using a higher O_2 concentration than that used for Figure 2, and the additional peaks provided more detailed fingerprints to illustrate differences in the gasoline constituents.

Figure 6 compares HWCID chromatograms for a Regular Grade of one brand Gasoline versus a Premium Grade of another brand Gasoline. The chromatograms were very similar except for the earliest eluting peaks. Brand A Regular clearly had a greater percentage of very volatile constituents than did the Brand B Premium sample.

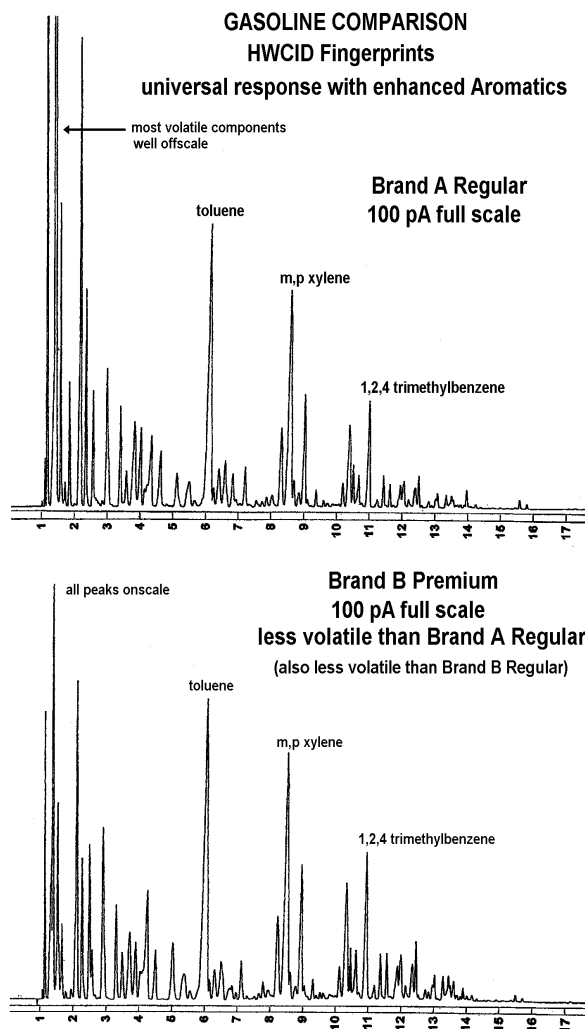


Figure 6. Same chromatographic conditions as Figure 5.

Figures 7 and 8 compare CCID and HWCID chromatograms for Premium and Regular Grades of the same brand of Gasoline. These data reflect Summer Blends of Gasoline versus previous data which referred to Winter Blends.

In figure 7, a comparison of relative peak amplitudes indicated that both Premium and Regular Grades had about the same ratios of C7 & C8 relative to Ethanol, and that the ratios of C6, C9, C10, Methyl Heptane, and Methyl Octane relative to Ethanol were all higher in the Premium Grade sample versus the Regular Grade sample.

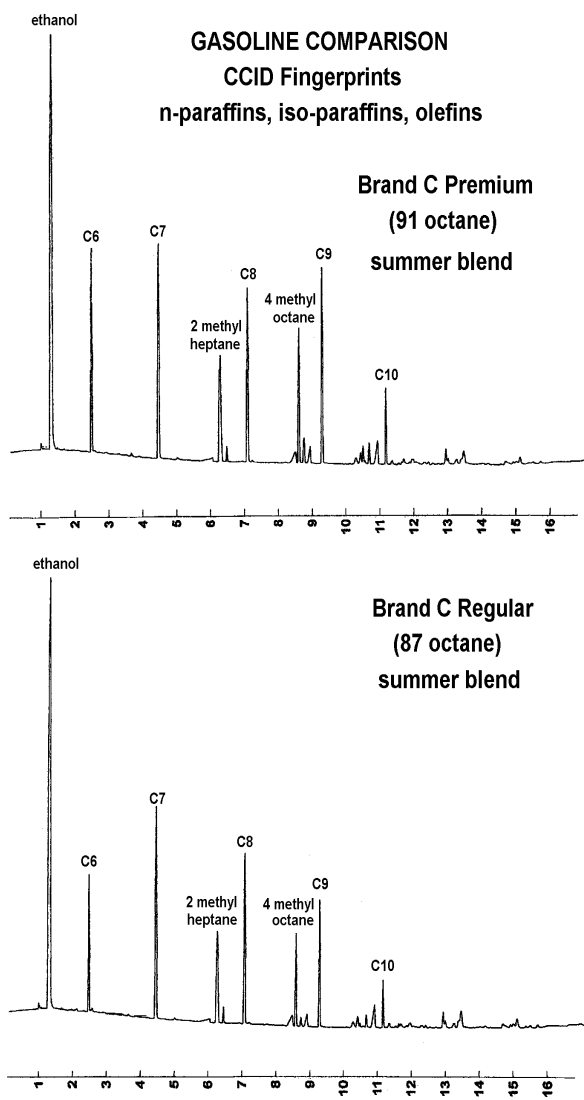


Figure 7

HWCID chromatograms do not have the simplifying selectivity of CCID chromatograms. Nevertheless, there is enough difference between HWCID chromatograms and FID chromatograms to allow some differences between gasoline samples to be ascertained. This is demonstrated in Figure 8 where there were at least places in the Premium versus Regular Grade chromatograms where there were evidenced some larger peaks in the Regular Grade chromatogram.

In summary, CCID and HWCID are two inexpensive variations of NPD equipment that provide differentiation of the constituents in different type gasoline samples. Gasolines are very complex samples, and the information demonstrated in this report could not easily have been obtained using just a universally responding FID detector.

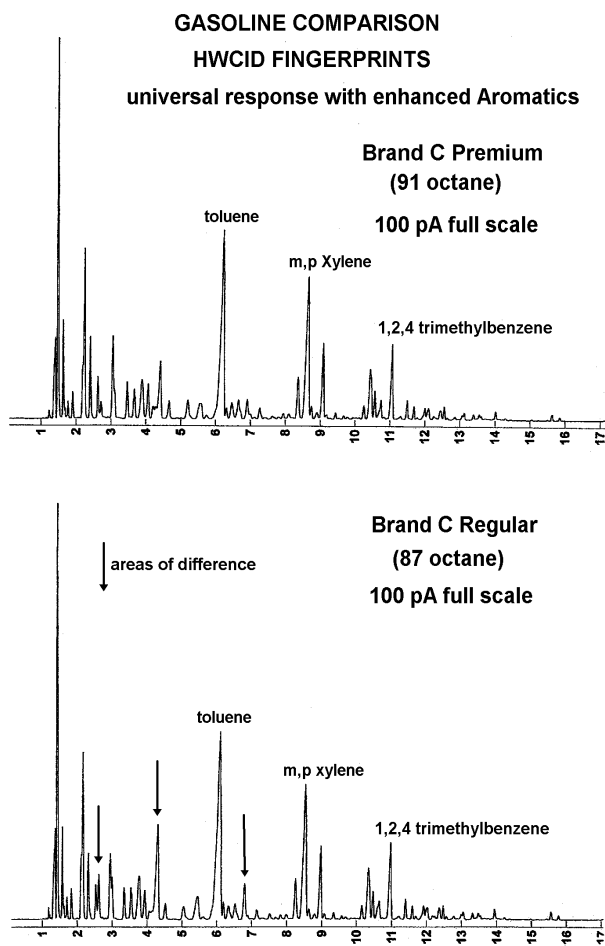


Figure 8.