

SELECTIVE TID-1 THERMIONIC DETECTION OF OXYGENATES AND HIGH CONCENTRATION HYDROCARBONS AS RELATED TO ANALYSES OF PETROLEUM AND BIOFUELS

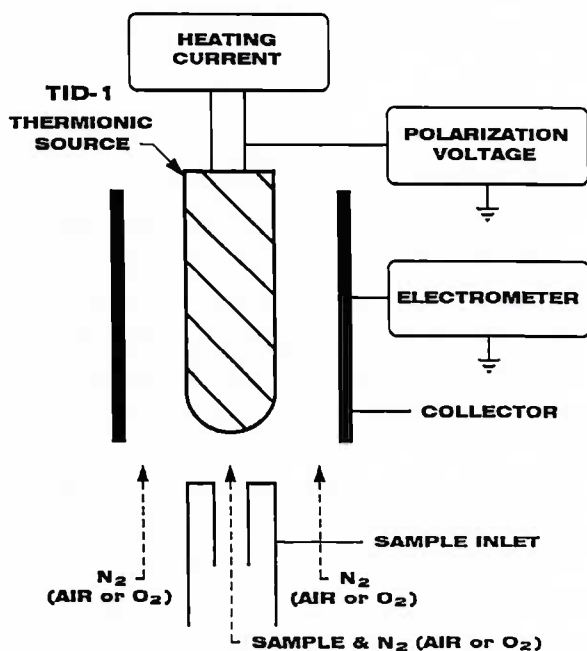
TID-1 Thermionic Surface Ionization is a relatively simple Gas Chromatography detection method that provides selective responses and chromatographic peak patterns quite different than any other type GC detector. A TID-1 detector is comprised of a 1/16 inch diameter ceramic coated ionization source optimally located on the axis of a concentric cylinder collector electrode. The TID-1 ionization source contains within it a wire core that allows it to be electrically heated to typical operating temperatures in the range of 400 - 600°C, and it is polarized at a negative voltage relative to the collector electrode. Incoming samples impact the heated ion source, and compounds containing certain types of electronegative atoms or functional groups form negative ion species that move through the surrounding gas to the collector. The ionization

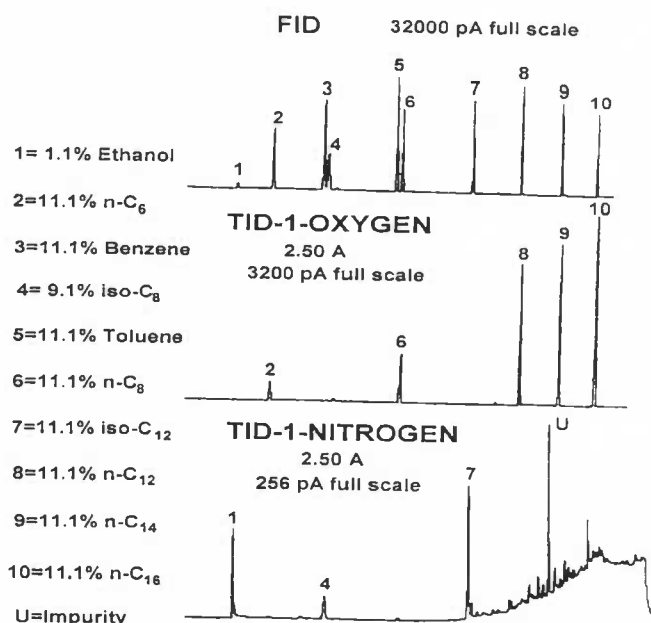
process can be extremely selective, and the type compounds detected can depend on whether the detector gas environment is inert Nitrogen or an oxidizing environment of Air or Oxygen.

While TID-1 detection can be extremely sensitive to minute traces of compounds containing strong electronegative functional groups or atoms like NO₂ or Halogens, the focus of this report is the selective detection of Oxygenates and high concentration Hydrocarbons as these are of current high interest due to developments of new petroleum and bio fuels. Enclosed in this report is a library of chromatograms illustrating TID-1 capabilities in this field of chemical analysis.

TID-1 detection is easily and inexpensively implemented on Agilent 6890/7890 GC models by a simple modification of Agilent's NPD equipment. For TID-1 detection, a TID-1 type ion source is substituted for the NP ion source, and the detector gases are changed to Nitrogen, Air, or Oxygen, or some combination thereof. While Agilent's NPD electronics suffice to achieve selectivity, 10 times better signal-to-noise can be achieved by substituting a stand-alone DET Current Supply for Agilent's Bead Voltage as the means of heating and polarizing the ion source. Most of the Agilent data enclosed in this report used the DET supply.

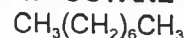
TID-1 detection has also been implemented on both Thermo Scientific and SRI Instruments GC models, again by substituting a TID-1 ion source into NPD equipment and supplying the appropriate detector gases. However, the original detector hardware structures on both the Thermo and SRI GC models are not the most optimum design for thermionic detection, so DET has developed better retrofit hardware for both these brand instruments.





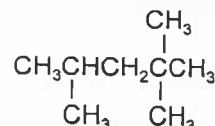
HYDROCARBON TEST SAMPLE
OCTANE & DODECANE COMPOUND STRUCTURES

n-OCTANE

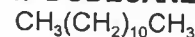


iso-OCTANE

(2,2,4-TRIMETHYLPENTANE)

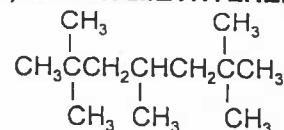


n-DODECANE



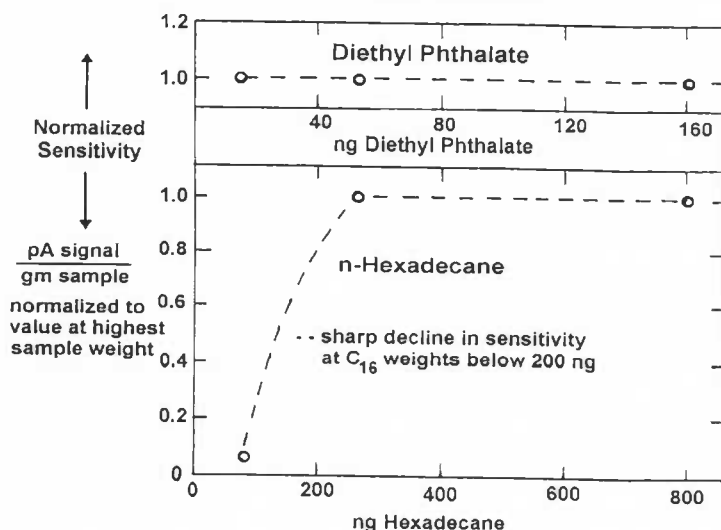
iso-DODECANE

(2,2,4,6,6-PENTAMETHYLHEPTANE)

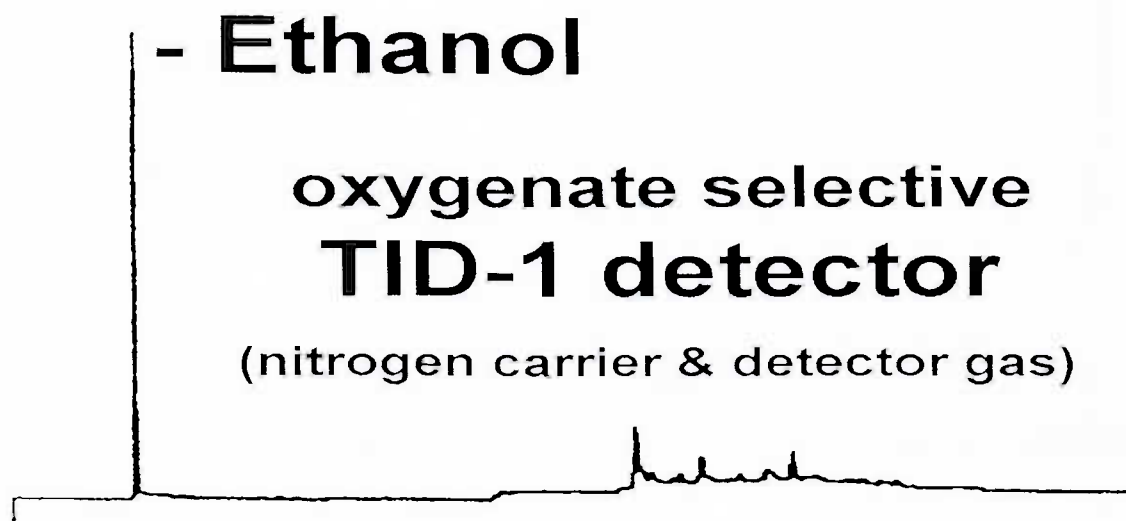
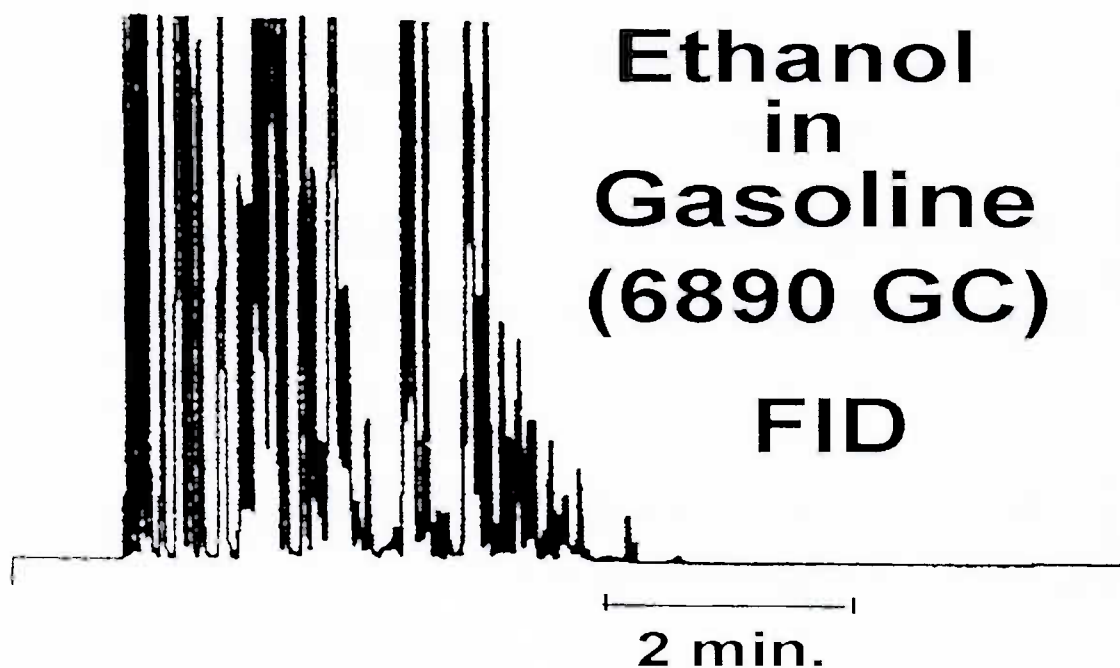


This sample illustrates the basic TID-1 response to high concentrations of Hydrocarbons. In a detector gas environment containing Oxygen, TID-1 response increased in magnitude correlated with the number of Methylene (CH₂) functional groups in linear chain Alkanes. In an inert detector gas of Nitrogen, TID-1 response correlated with the number of branched Methyl (CH₃) functional groups. TID-1-Nitrogen Hydrocarbon responses were much lower magnitude than TID-1-Oxygen responses, and TID-1-Nitrogen showed traces of Oxygenates (peak 1, Ethanol) and other Heteroatom compounds (unidentified peak U) with responses greatly magnified versus the Hydrocarbons. The aromatic hydrocarbon compounds, Benzene and Toluene, did not exhibit any TID-1 response in either Nitrogen or Oxygen gas environments.

TID-1-AIR



TID-1 response to Hydrocarbons in an Oxygen containing environment exhibits a threshold in sample amount below which the response drops off sharply. This indicates that the TID-1 response in the presence of Oxygen is due to a burst of gas phase ionization as each high concentration Hydrocarbon peak momentarily ignites a flame as it impacts the hot, catalytically active TID-1 surface. TID-1 responses versus different compound structures can provide interesting insight on fundamental processes involved in combustion ignition of petroleum and biofuels.



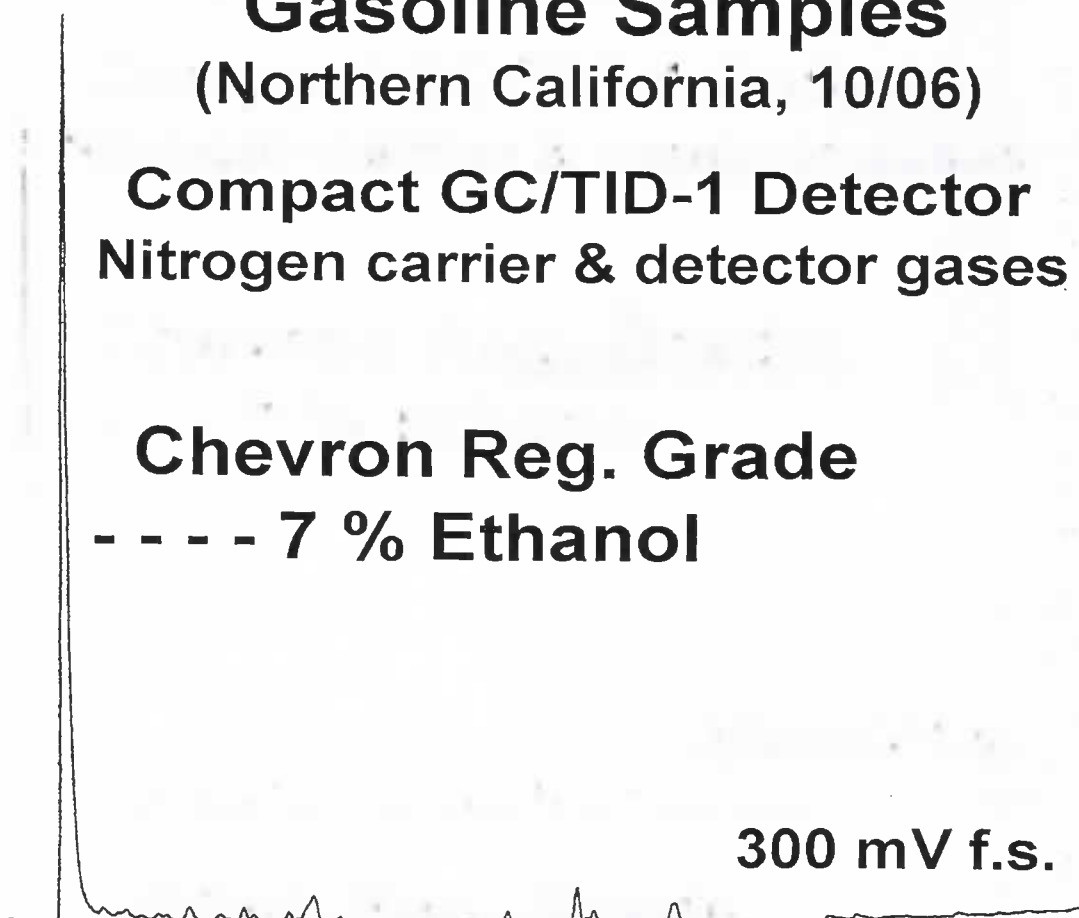
Selective detection of Ethanol in Gasoline using TID-1 surface ionization in a detector gas environment of Nitrogen. This is a signature chromatogram demonstrating how a selective detector can greatly simplify a chemical analysis. Only a single Nitrogen gas is required for both GC carrier and detector gases, and a short analysis time suffices because overlapping Hydrocarbon peaks are just not detected.

Gasoline Samples

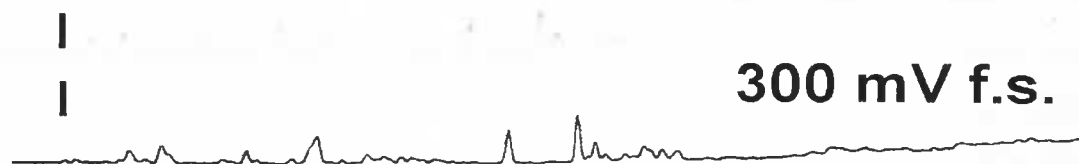
(Northern California, 10/06)

Compact GC/TID-1 Detector
Nitrogen carrier & detector gases

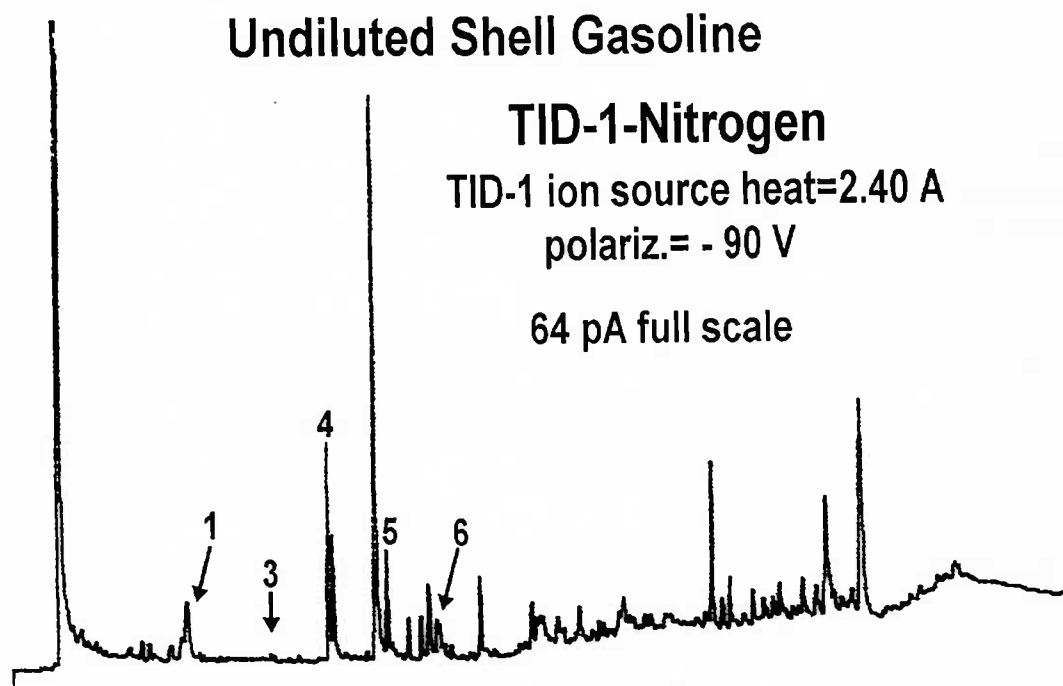
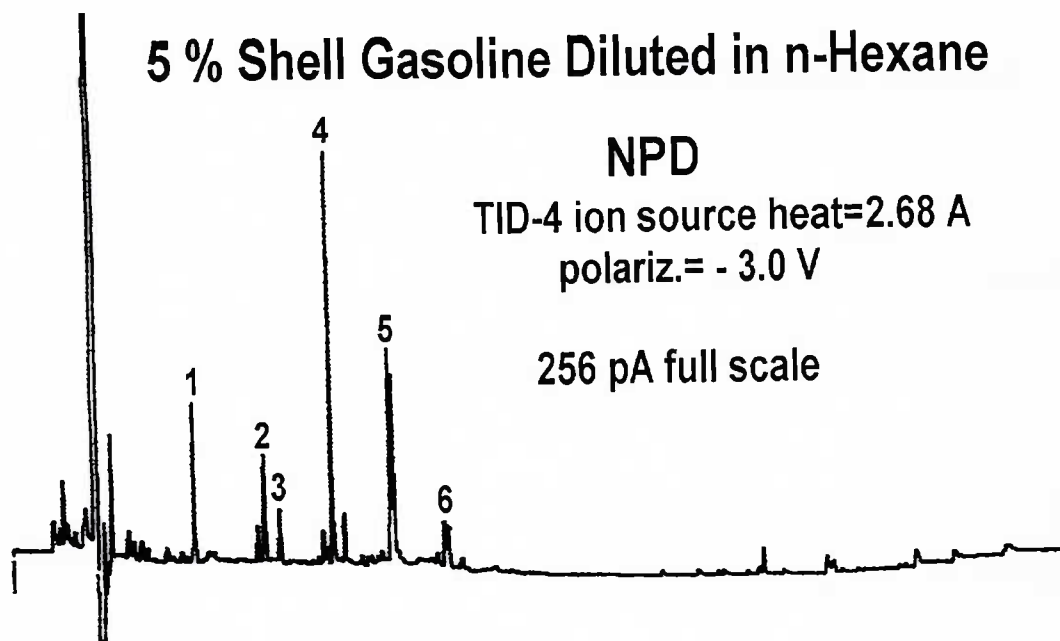
Chevron Reg. Grade
- - - - 7 % Ethanol



Shell Reg. Grade
less than 0.05 % Ethanol

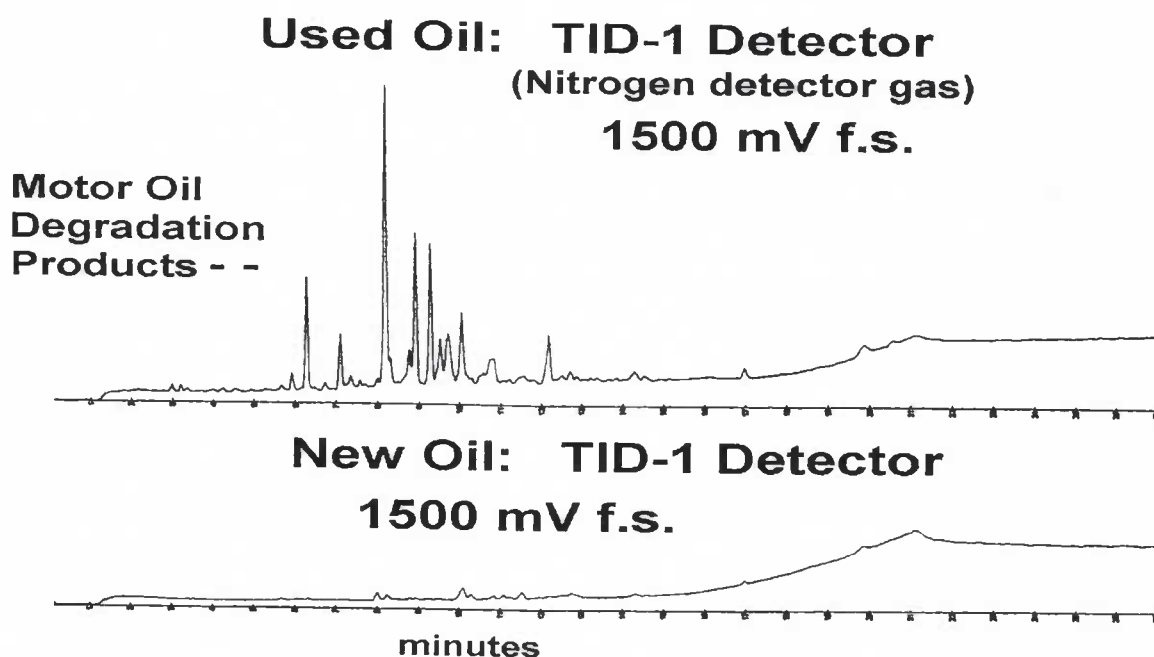
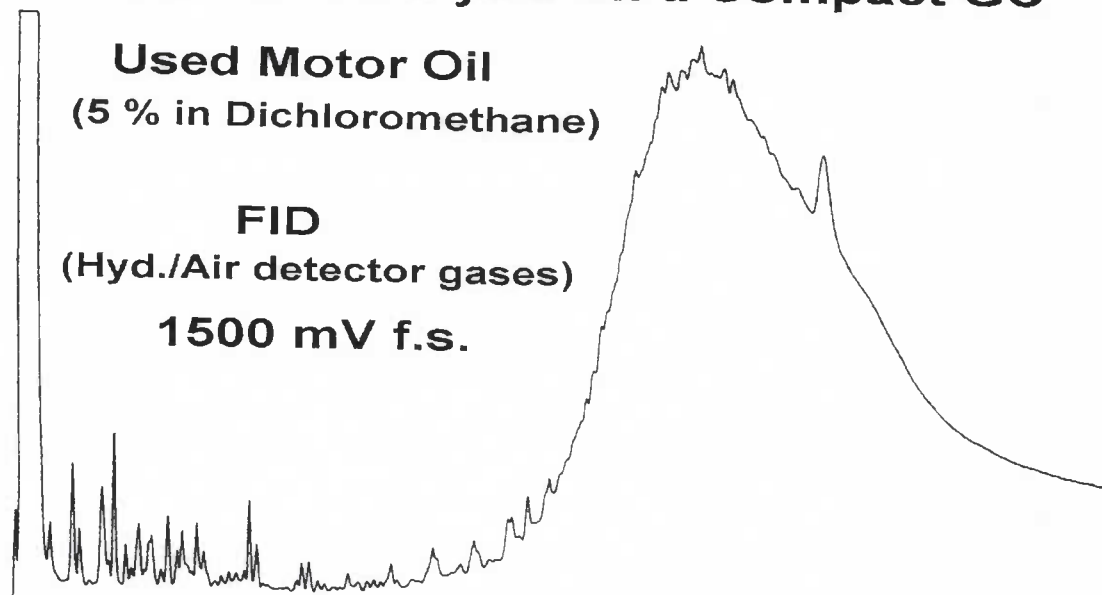


2006 Gasoline samples. Chevron had Ethanol additive, while Shell did not. Hydrocarbon discrimination was sufficient to determine that there was no peak at Ethanol retention time corresponding to 0.05 % or larger Ethanol.

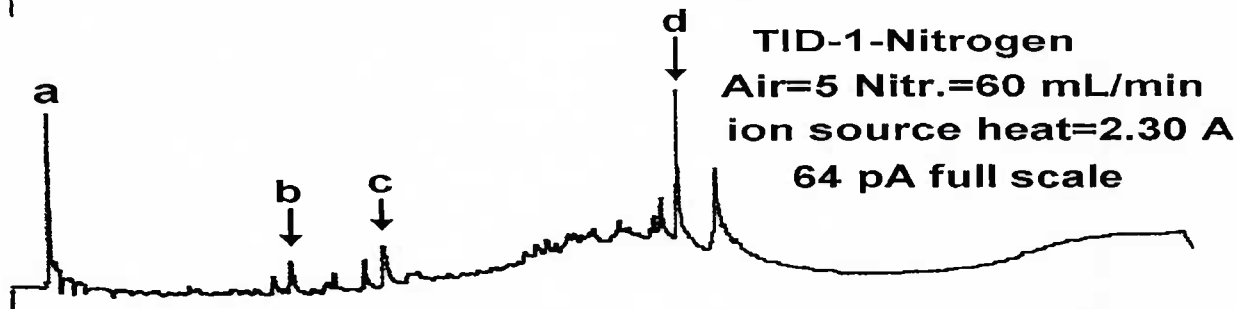
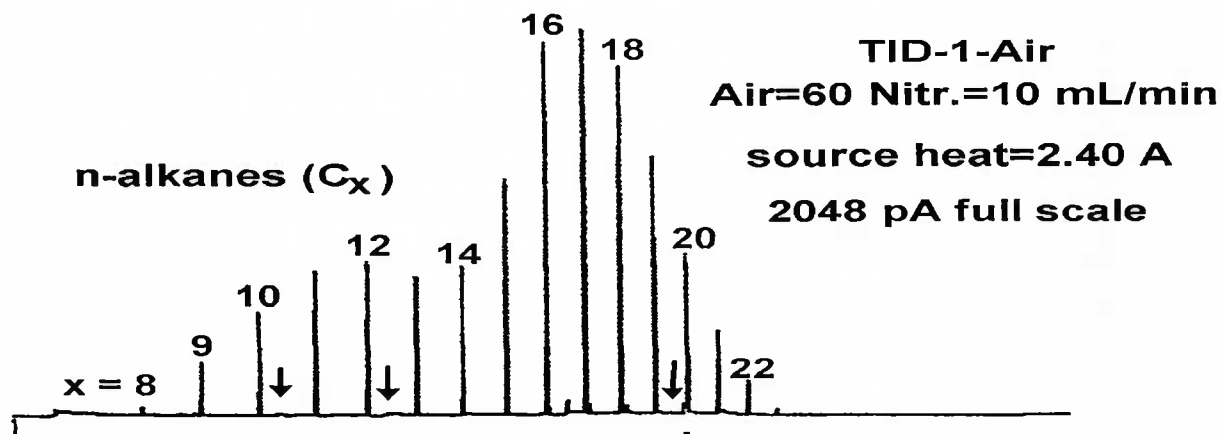
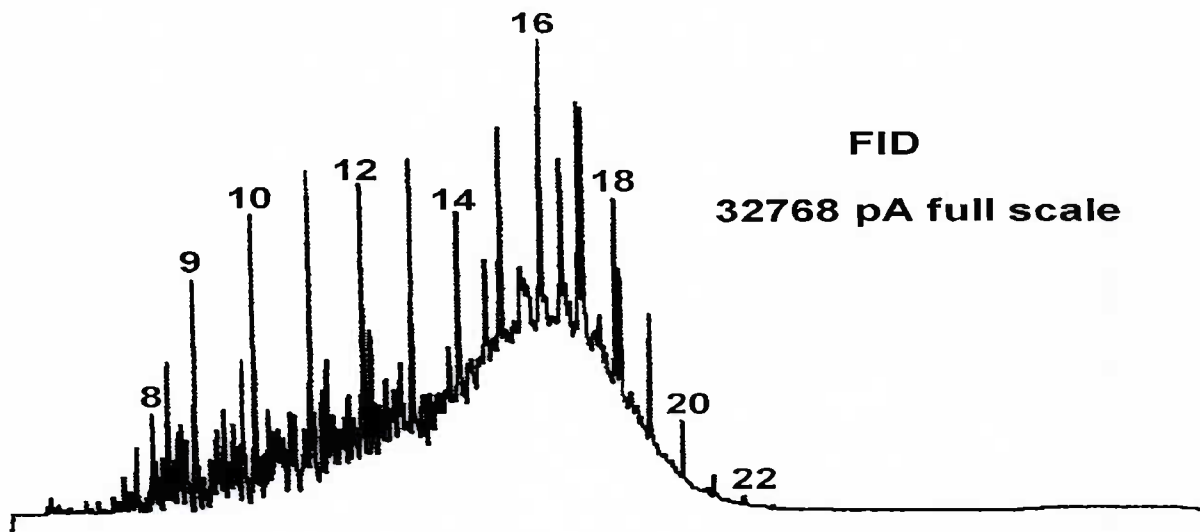


NPD detection of Nitrogen containing detergents added to gasoline - dilution of sample minimizes interferences from gasoline Hydrocarbons. TID-1 detection provides a different gasoline fingerprint. Thermo GC.

Motor Oil Analysis on a Compact GC



Selective TID-1 ionization in a Nitrogen detector gas environment reveals motor oil degradation products that build up with time as the oil is used. TID-1 monitoring of car oil vs. use can be very simple - take oil drop from car dipstick, dilute 1:3 in n-Hexane, and inject into GC. These data were obtained with interchangeable FID and TID modes on a compact SRI 310 GC equipped with DET detector hardware and a DET stand-alone Current Supply.

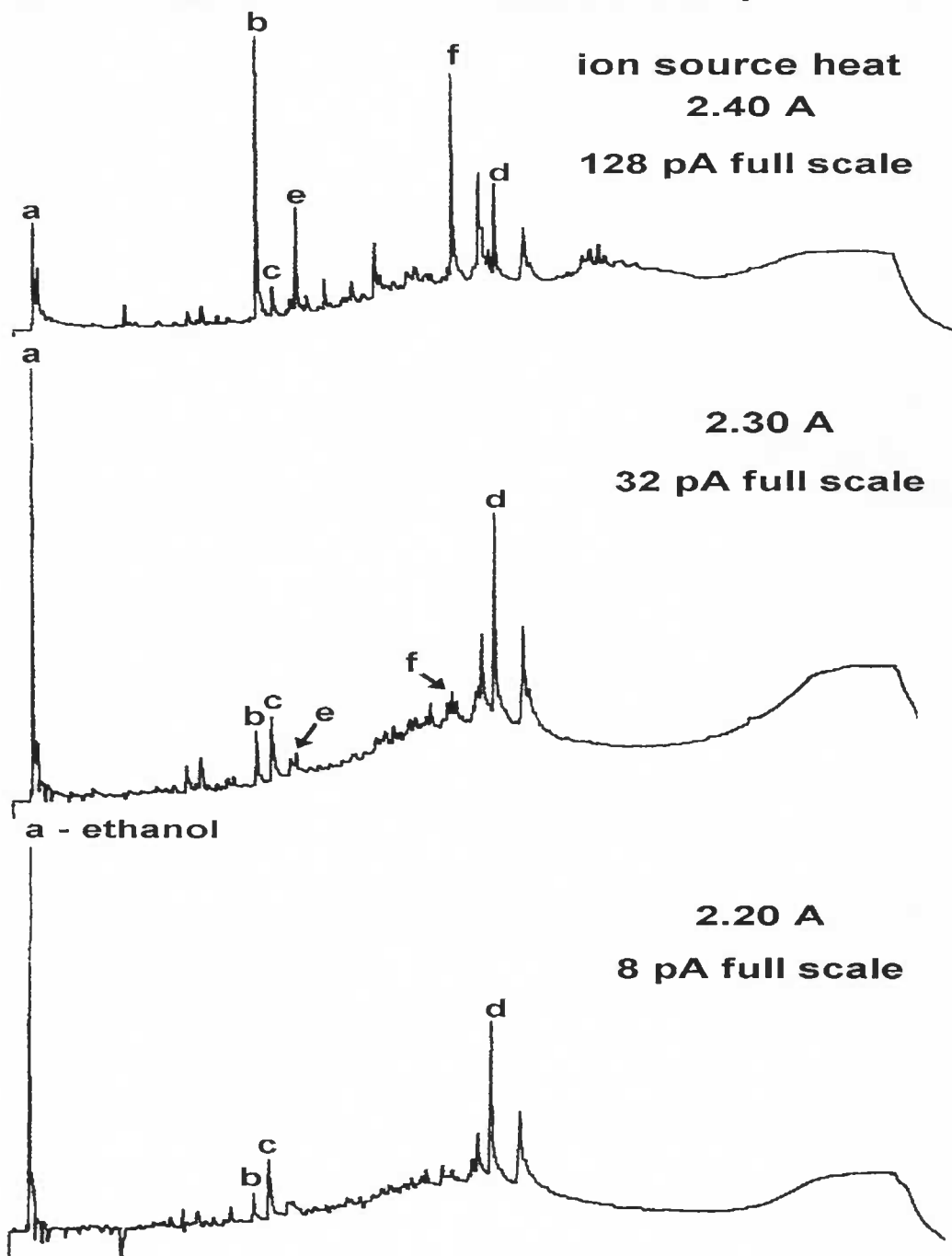
AUTO DIESEL SAMPLE (Valero, 04/09, N. Calif.)

TID-1-Air selectively detected the linear Alkanes. Peak "a" in the TID-1-Nitrogen chromatogram was Ethanol, but other peaks not yet identified.

Agilent 6890 GC. TID data from 6890 NPD equipment modified with DET TID-1 Ion Source and stand-alone DET Current Supply.

TID-1- Nitrogen

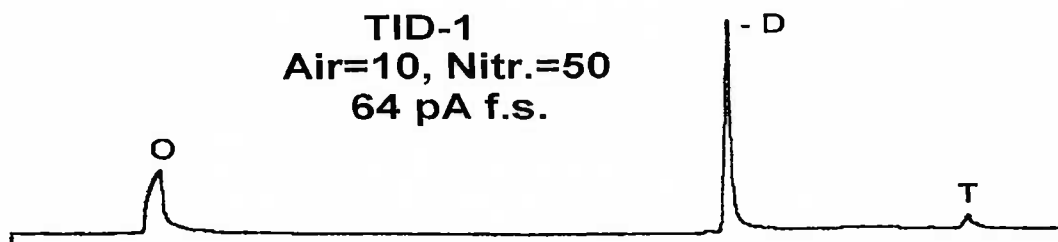
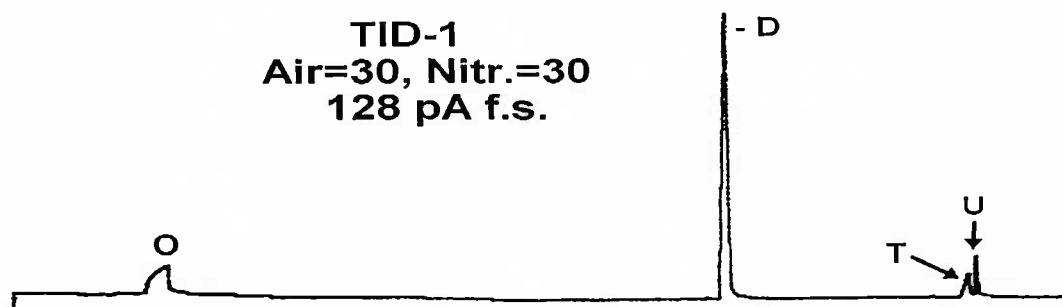
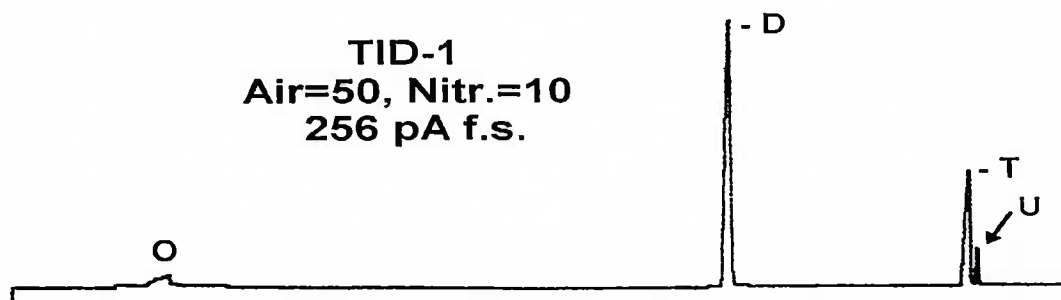
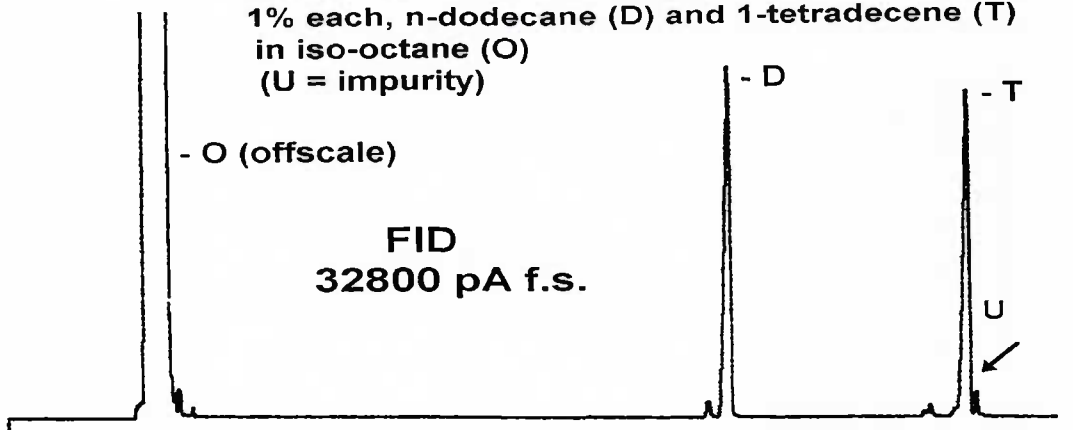
Auto Diesel Sample



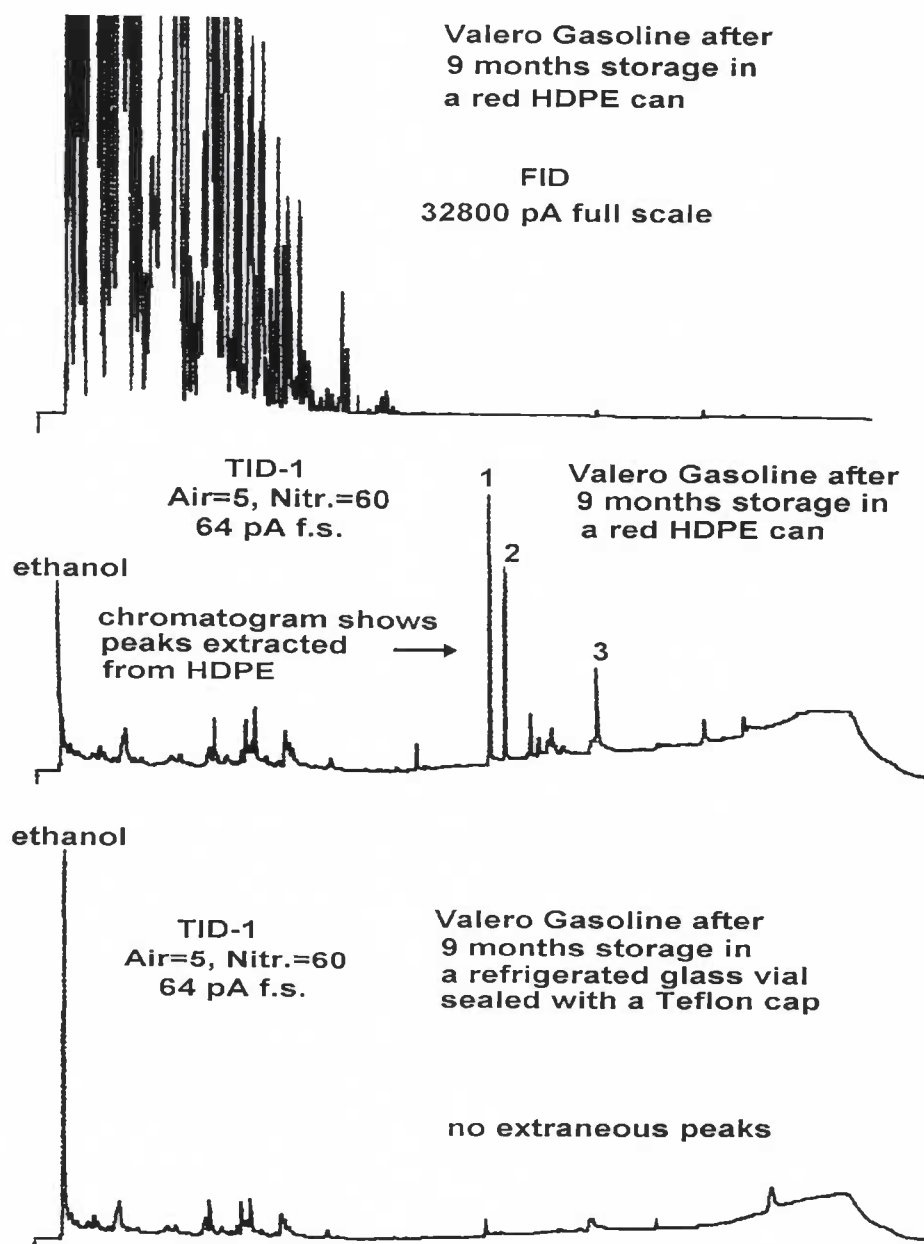
Undiluted Auto Diesel Sample (Valero, 04/09, N. Calif.). Agilent 6890 NPD with DET TID-1 Ion Source and DET Current Supply and Nitrogen detector gas. Data show how chromatogram peak patterns change with increasing ion source temperature.

Alkane vs. Alkene Response Comparison

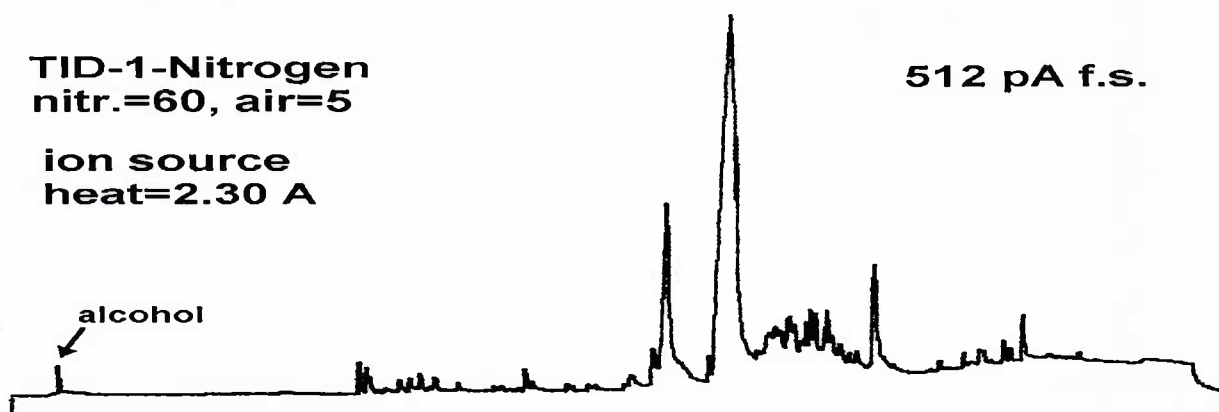
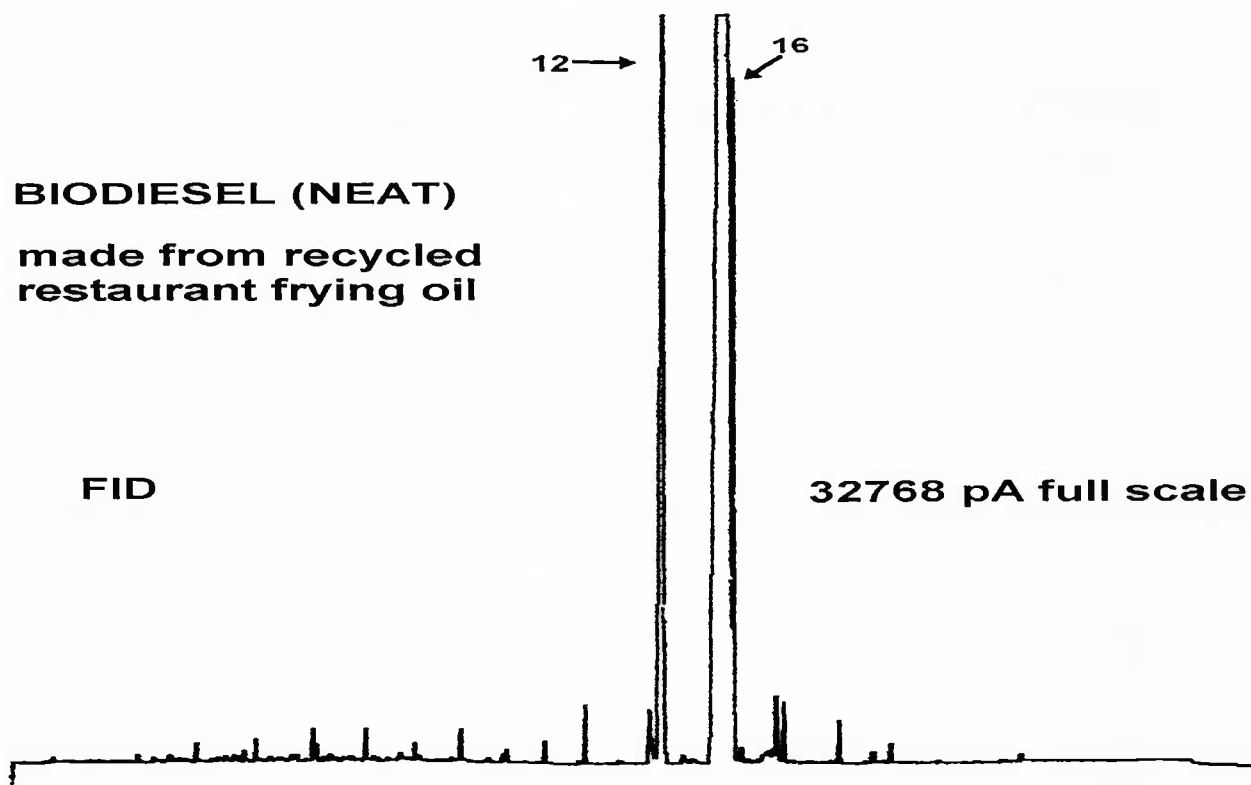
1% each, n-dodecane (D) and 1-tetradecene (T)
in iso-octane (O)
(U = impurity)



In a detector gas environment containing Oxygen, TID-1 ionization responds to CH_2 functional groups in high concentrations of linear Alkanes, but has significantly lower response to linear Alkenes which have a carbon double bond in addition to CH_2 groups.

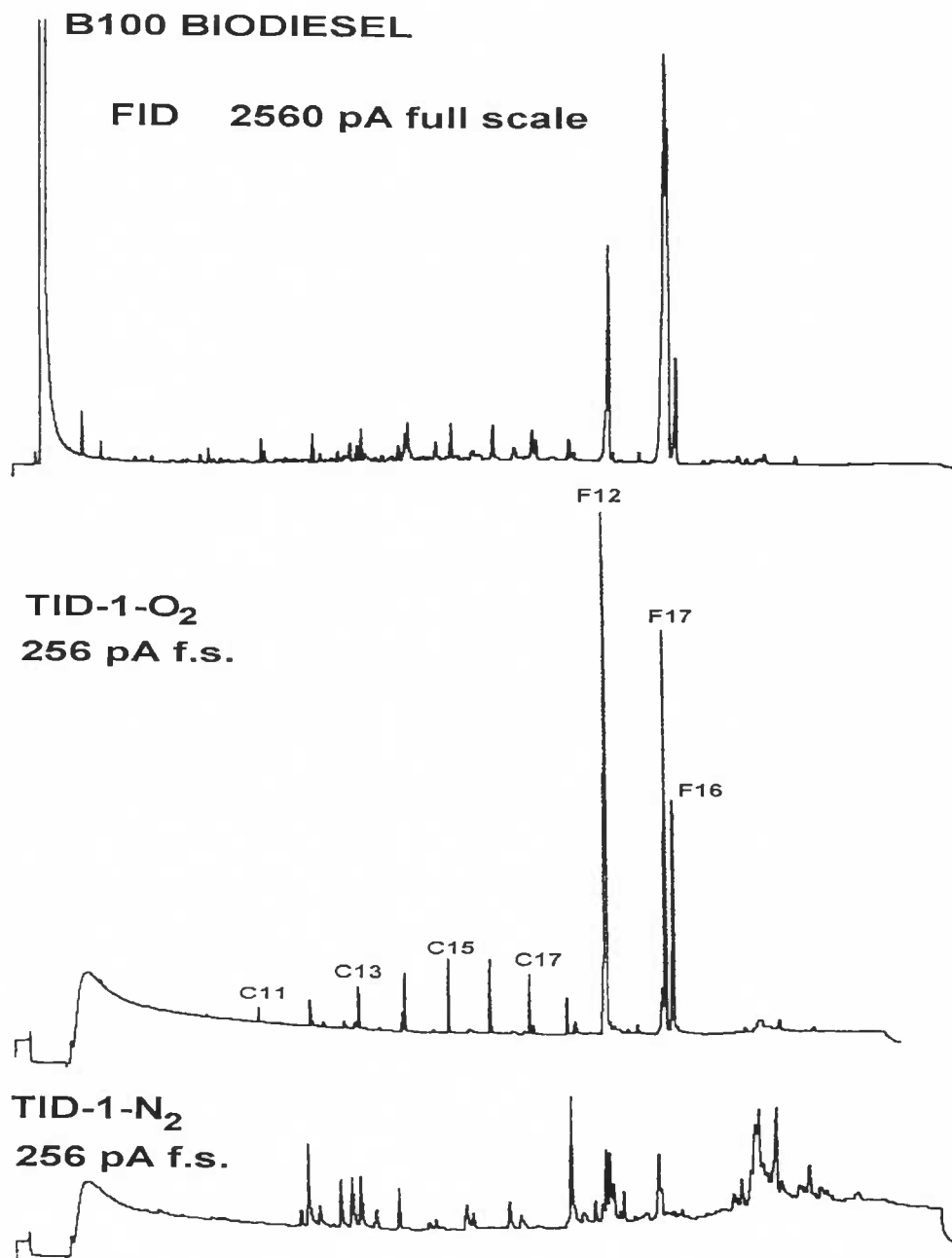
Gasoline Extraction of Storage Container Constituents

In a detector gas environment of predominantly Nitrogen, excellent Hydrocarbon discrimination of TID-1 ionization allows Gasoline to be used as an extracting solvent. TID-1 chromatogram of Gasoline stored in a commonly used HDPE can exhibits peaks extracted from the container. Retention time of peak 1 corresponds to that of DiethylPhthalate. Note that extracted peaks are not detected in the FID chromatogram.

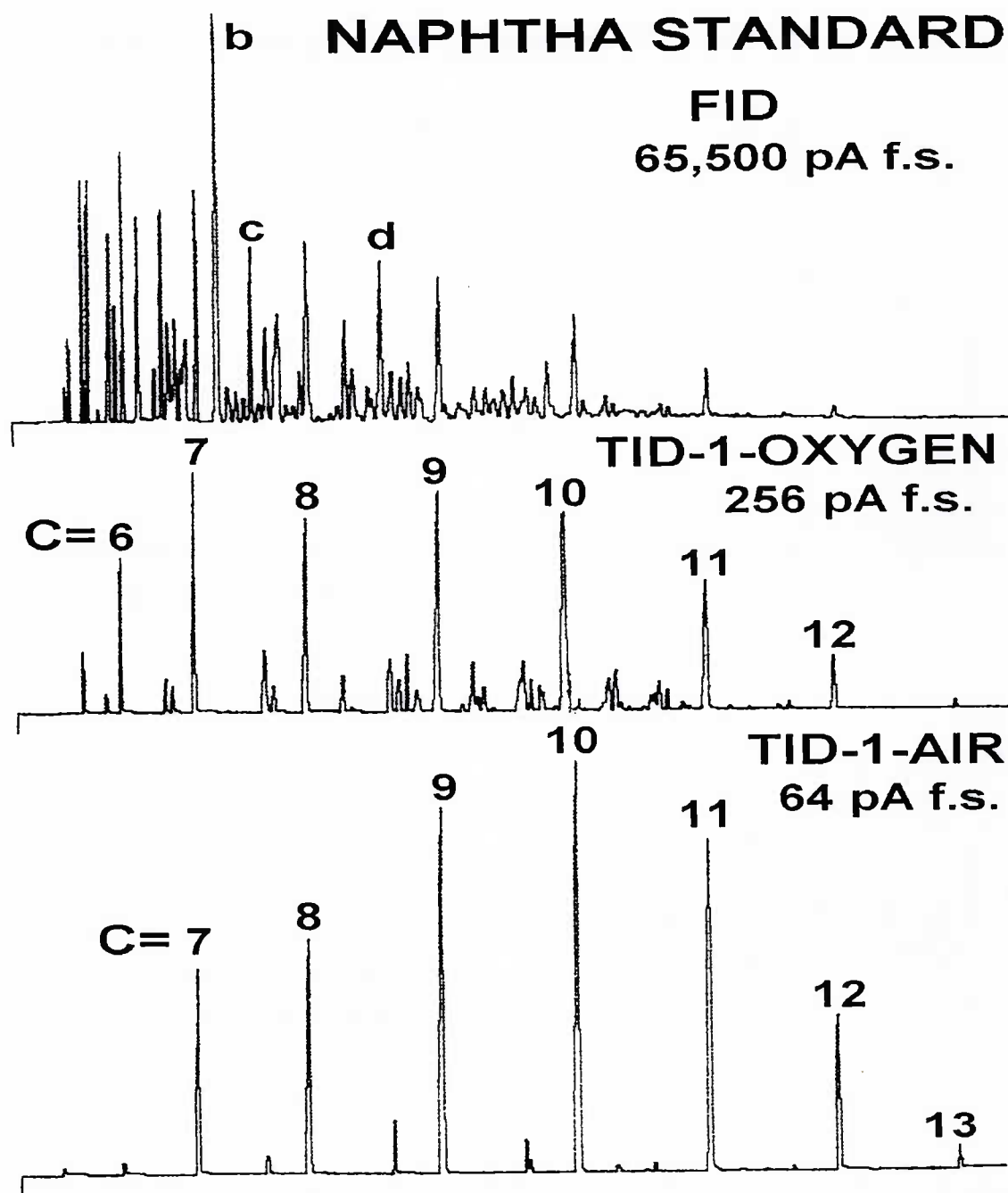


UNDILUTED (NEAT) BIODIESEL SAMPLE

Alcohol peak in TID chromatogram is n-Propanol. Broad detector signals correspond to poorly resolved unsaturated FAMES. Peaks 12 and 16 are Palmitic and Stearic saturated FAMES, respectively.

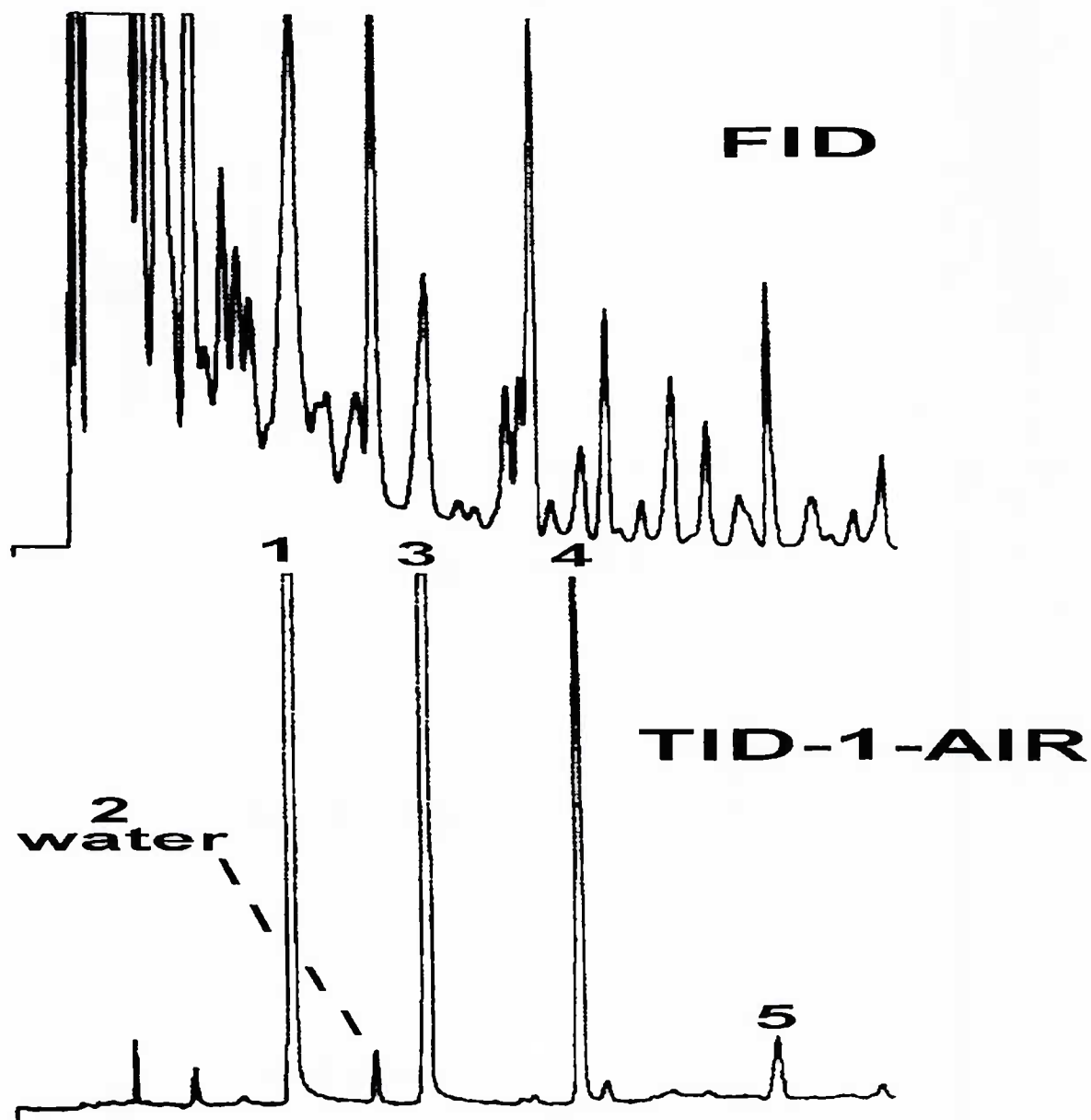


Comparison of FID and TID chromatograms of a 20mg/mL sample of B100 Biodiesel in a Methylene Chloride solvent. Cx nomenclature refers to linear Alkanes, F12, F16, and F17 refer to Palmitic, Stearic, and Oleic FAMES, respectively. TID-1-N₂ peaks are not yet identified.



Agilent 6890 GC. TID-1 ion source in 6890 NPD hardware with DET Current Supply for ion source power. C=x indicates Carbon number in linear Alkanes; b = Methyl-cyclohexane & cis-1,2-Dimethylcyclopentane; c = Toluene; d = m-Xylene & p-Xylene.

NAPHTHA STANDARD

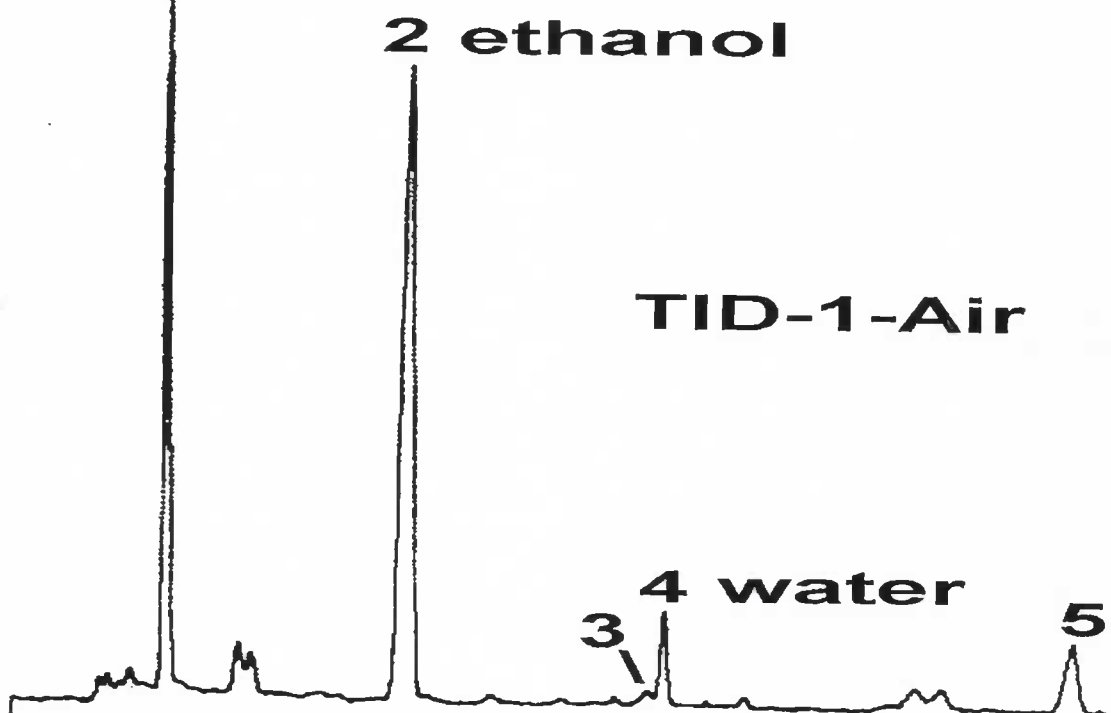
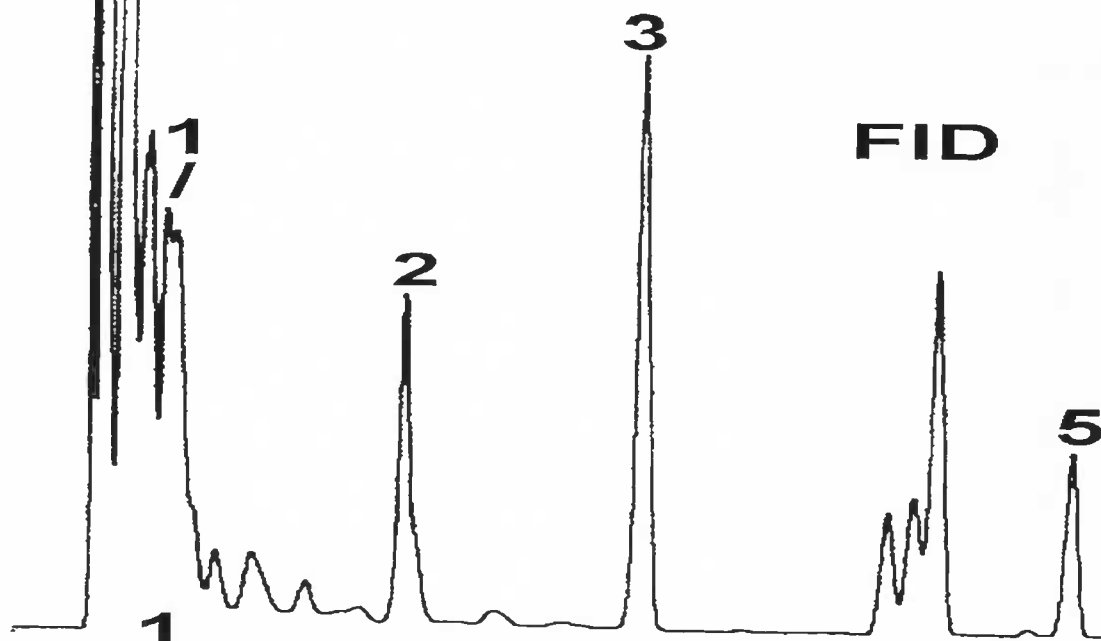


TID-1-Air DETECTION OF WATER IN A NAPHTHA STANDARD

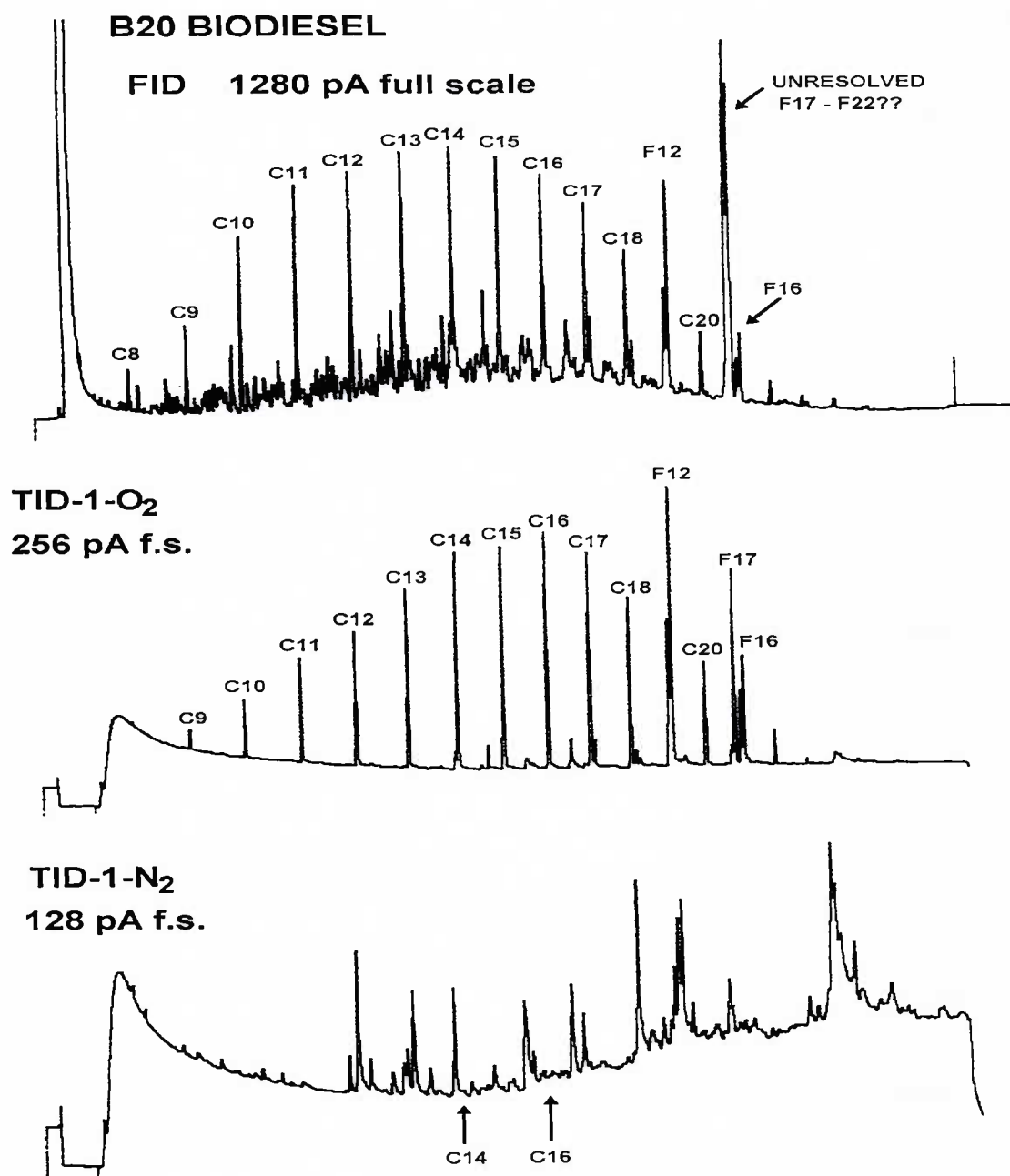
Peaks labeled 1, 3, and 4 in the TID chromatogram refer to detection of CH_2 functional groups in the straight chain Alkanes n-C_{10} , n-C_{11} , and n-C_{12} , respectively.

Water in Gasoline

(87 Octane, N. Calif., July 2004)

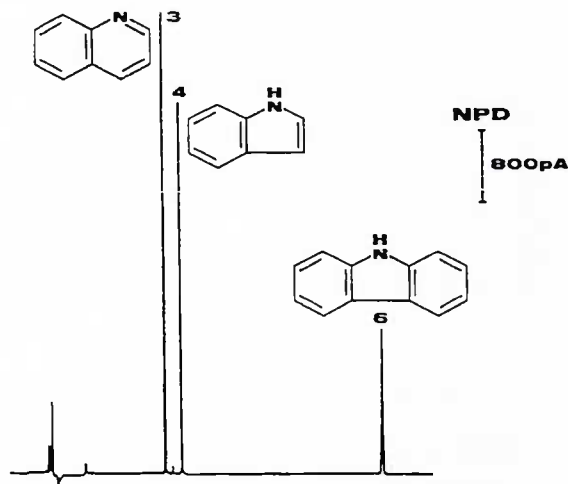
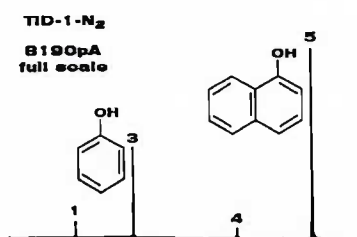
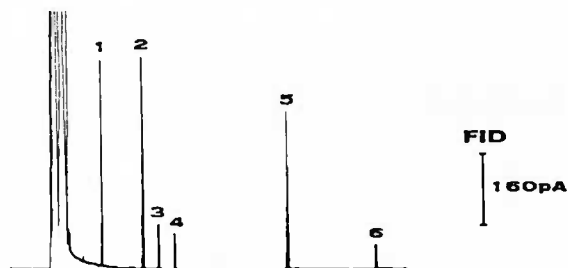
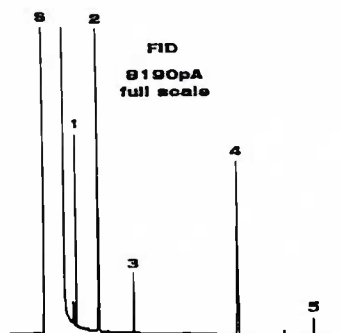


Unique TID-1 selectivity allows detection of Water in a complex Hydrocarbon matrix like Gasoline.



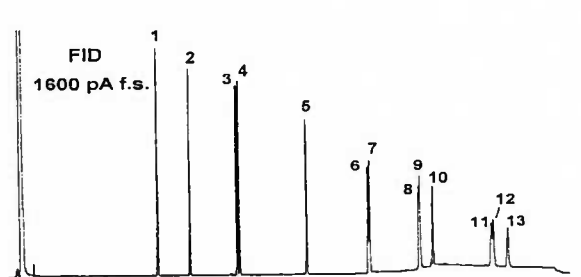
Comparison of FID and TID chromatograms of a 20mg/mL sample of B20 Biodiesel in a Methylene Chloride solvent. Cx nomenclature refers to linear Alkanes, Fx nomenclature refers to FAMES. F12, F16, and F17 are Palmitic, Stearic, and Oleic FAMES, respectively. TID-1-N₂ peaks are not yet identified.

OTHER TID-1 RESPONSES OF RELEVANCE TO PETROLEUM ANALYSES



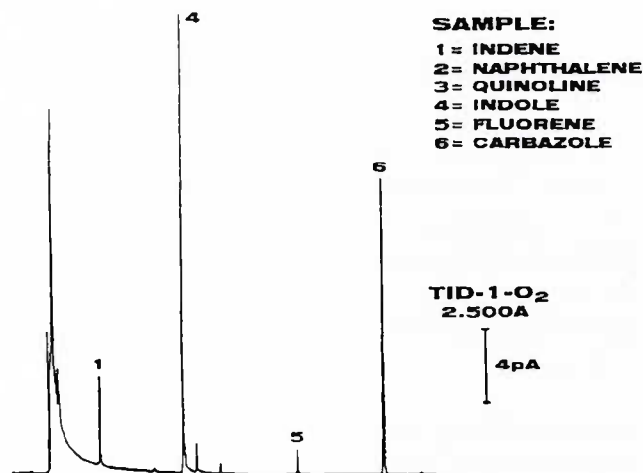
LARGE RESPONSE OF PHENOLS VS. ALCOHOLS

S=Benzene solvent, 1=260ppm Cyclopentanol,
 2=990ppm p-Xylene, 3=51ppm Phenol,
 4=350ppm n-Decanol, 5=51ppm 1-Naphthol



TID-1-Nitrogen
2.40 A
64 pA f.s.

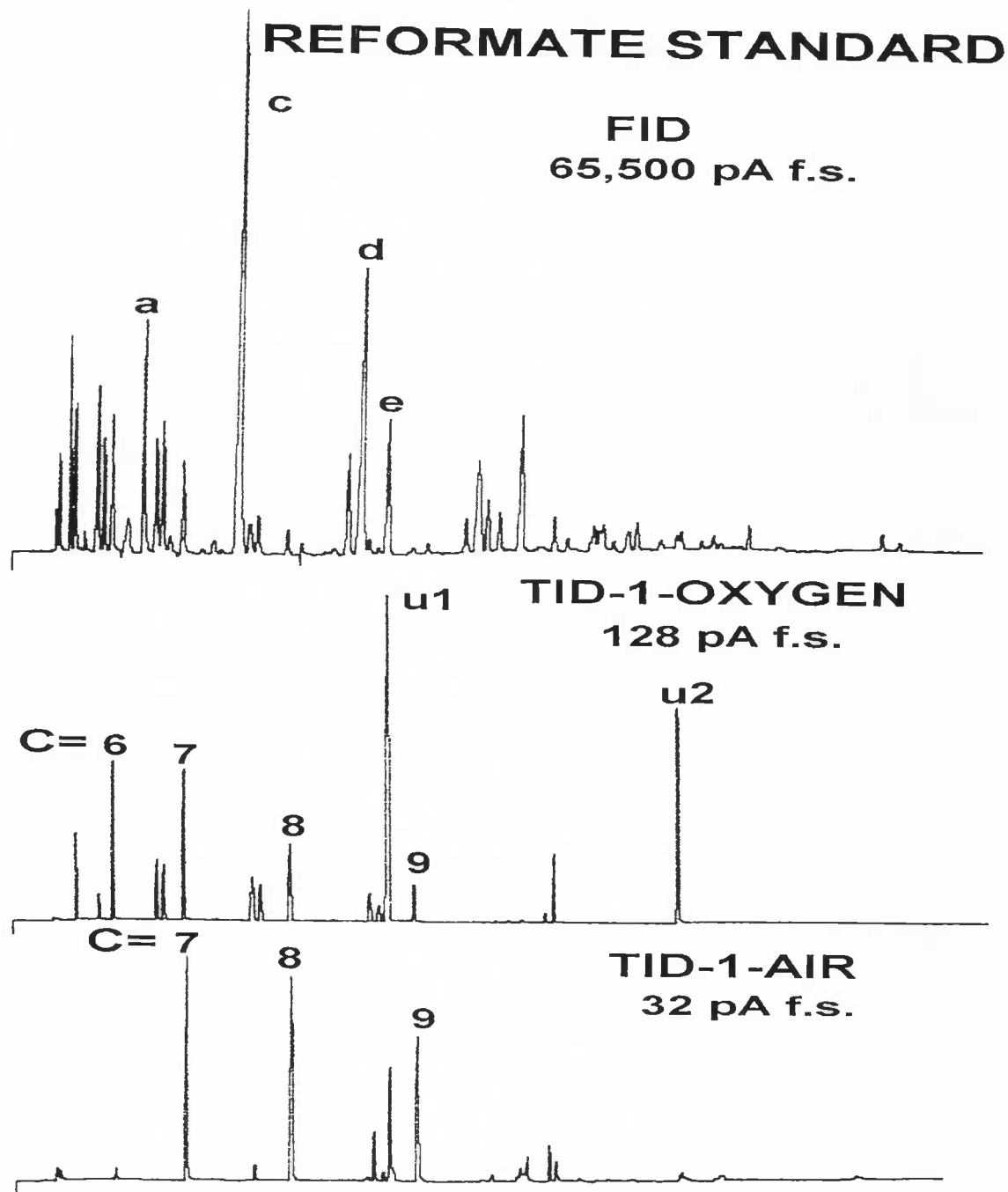
PAH (350ng each)
 1=Acenaphthylene
 2=Flourene
 3=Phenanthrene
 4=Anthracene
 5=Pyrene
 6=Benzo(a)anthracene
 7=Chrysene
 8=Benzo(b)fluoranthene
 9=Benzo(k)fluoranthene
 10=Benzo(a)pyrene
 11=Inden(1,2,3-cd)pyrene
 12=Dibenzo(a,h)anthracene
 13=Benzo(ghi)perylene



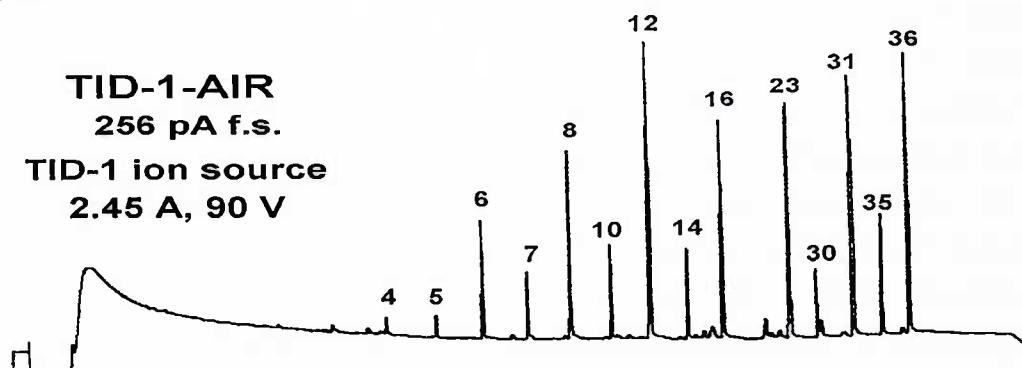
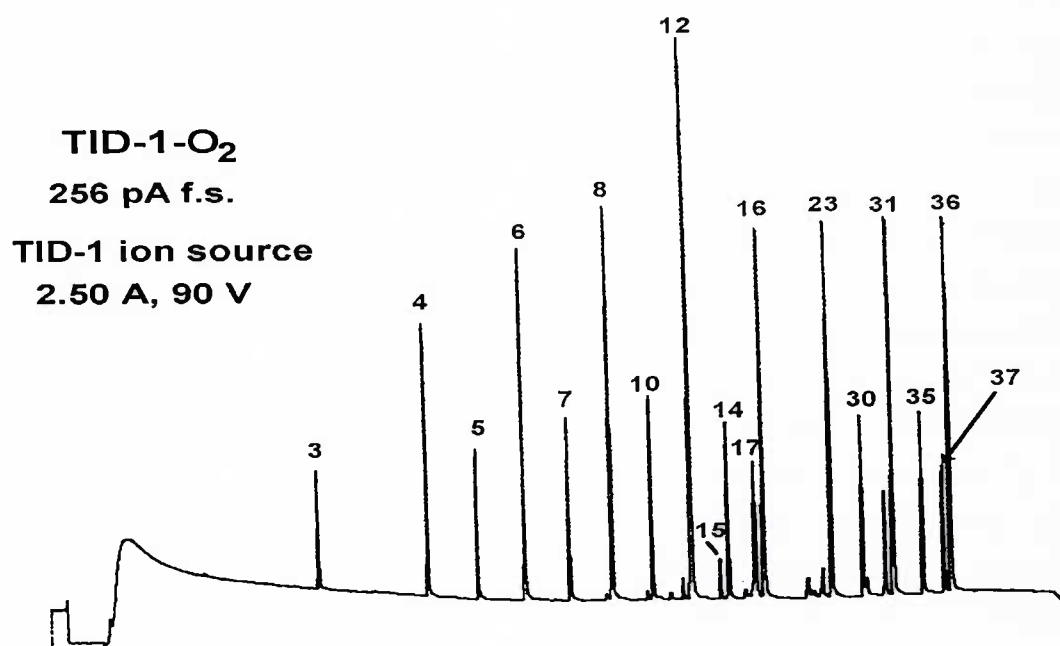
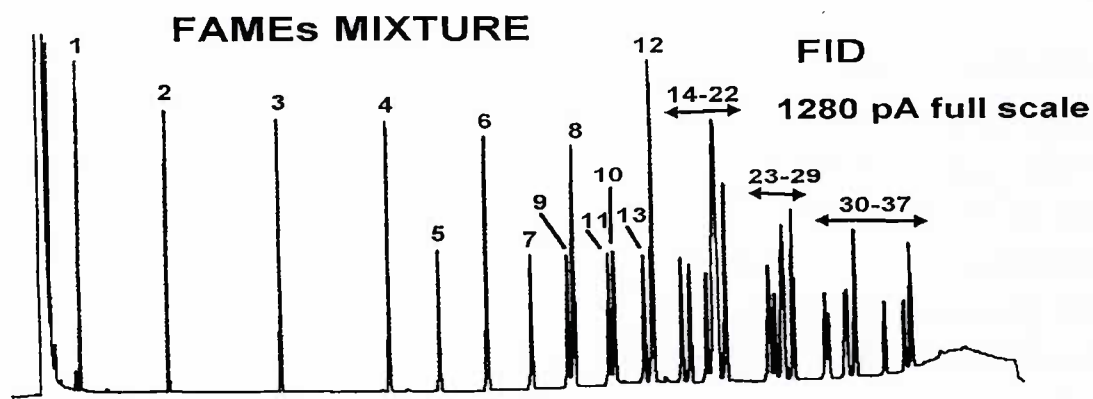
SAMPLE:
 1= INDENE
 2= NAPHTHALENE
 3= QUINOLINE
 4= INDOLE
 5= FLUORENE
 6= CARBAZOLE

SELECTIVE DETECTION OF THE 5 MEMBER HYDROCARBON RING STRUCTURE IN FLUORENE

SELECTIVE TID-1 DETECTION OF THE PYRROLE GROUP IN INDOLE AND CARBAZOLE VS. THE PYRIDINE GROUP IN QUINOLINE. ALSO TID-1 SELECTIVITY TO INDENE AND FLUORENE VS. NAPHTHALENE. 1=320ng Indene, 2=320ng Naphthalene, 3=78ng Quinoline, 4=66ng Indole, 5= 320ng Fluorene, 6=66ng Carbazole.

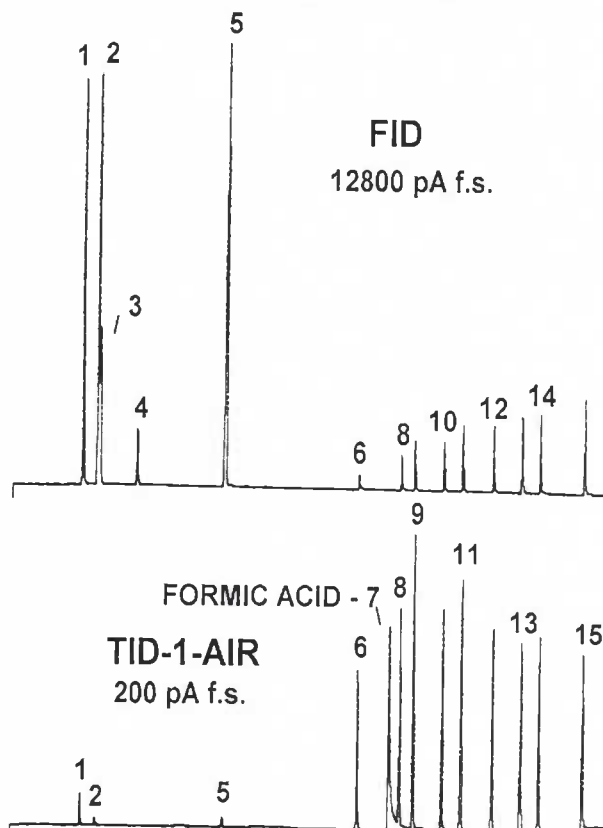


Agilent 6890 GC. TID-1 ion source in 6890 NPD hardware with DET Current Supply for ion source power. C=x indicates Carbon number in Linear Alkanes; a = Benzene; c = Toluene; d = m-Xylene & p-Xylene; e = o-Xylene; u1 & u2 = unidentified components (likely heteroatoms).



TID-1 detection of long chains of CH₂ groups in Fatty Acid Methyl Esters (FAMES).
DET Retrofit TID/FID Detector Hardware on Thermo Trace GC and Powered with
Thermo's NPD Electronics. Only Saturated FAME Compounds Detected with
TID-1-Air. Peak identities on back side.

CARBOXYLIC ACID SELECTIVITY

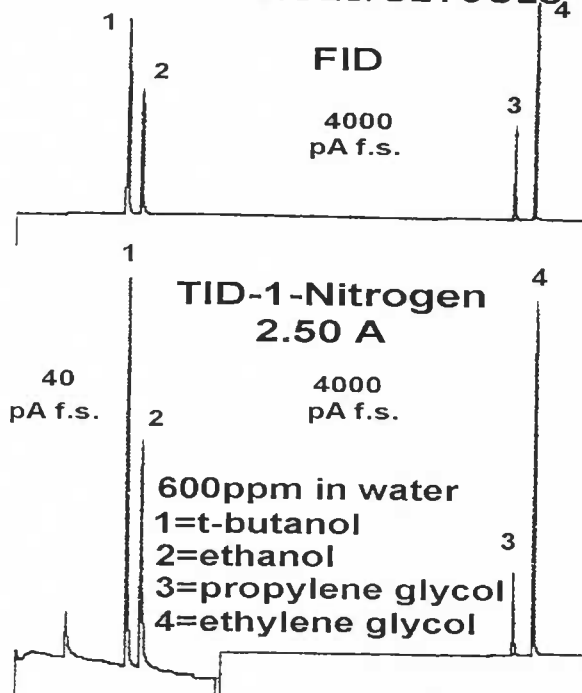


LARGE TID-1 RESPONSE TO CARBOXYLIC ACIDS VS. ALCOHOLS, INCLUDING RESPONSE TO FORMIC ACID WHICH AN FID DOES NOT DETECT. DETECTOR GAS ENVIRONMENT OF AIR HELPS SUPPRESS ALCOHOL RESPONSES RELATIVE TO THE ACIDS.

Sample in Water solution:

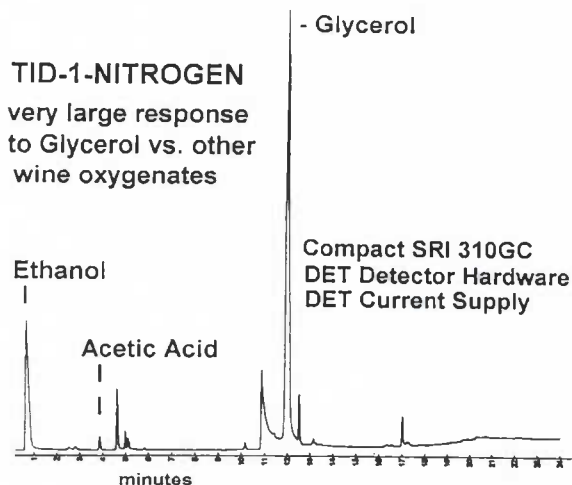
1=Ethanol (1%), 2=Ethyl Acetate (1%),
 3=Benzene (0.15%), 4=Toluene (0.1%),
 5=iso-Pentanol (1%), 6=Acetic Acid (0.1%),
 7=Formic Acid (0.1%), 8=Propionic Acid (0.1%),
 9=iso-Butyric Acid (0.1%), 10=Butyric Acid (0.1%),
 11=iso-Valeric Acid (0.1%), 12=n-Valeric Acid (0.1%),
 13=iso-Caproic Acid (0.1%),
 14=n-Caproic Acid (0.1%), 15=Heptanoic Acid (0.1%)

ALCOHOLS/GLYCOLS



LARGE TID-1 RESPONSE TO GLYCOLS VS. ALCOHOLS.

SHIRAZ WINE SAMPLE



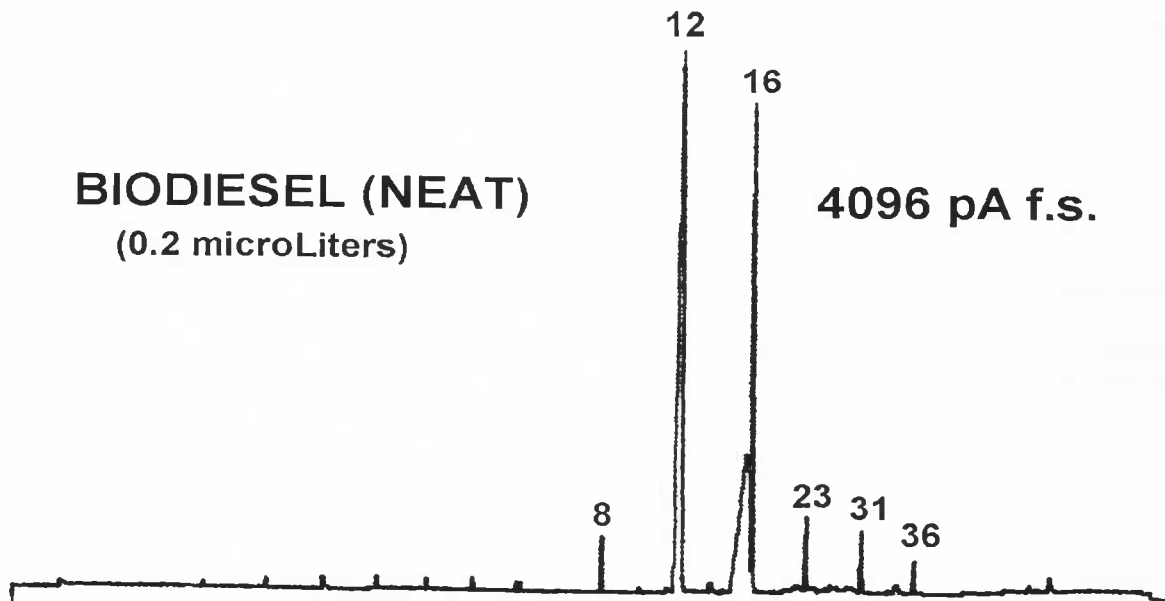
VERY LARGE RESPONSE TO GLYCEROL WITH TID-1 IONIZATION IN A NITROGEN ENVIRONMENT

TID-1-Air (air=50, nitr.=5)
ion source heat=2.30 A

Agilent 6890 GC

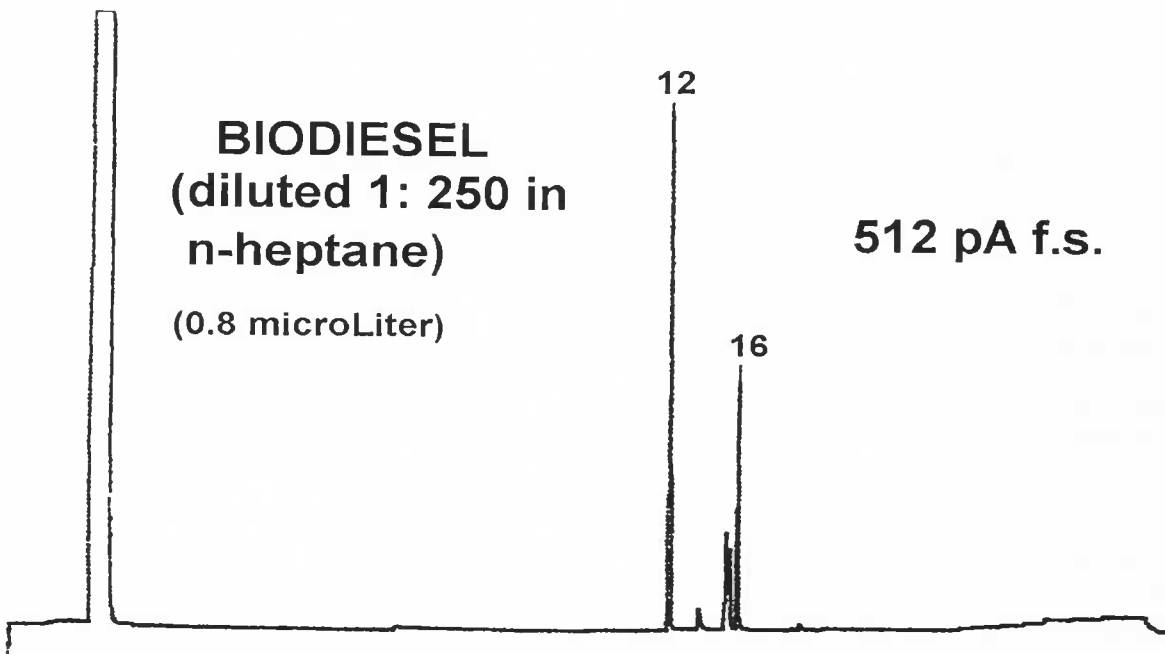
BIODIESEL (NEAT)
(0.2 microLiters)

4096 pA f.s.



BIODIESEL
(diluted 1: 250 in
n-heptane)
(0.8 microLiter)

512 pA f.s.



Agilent 6890 NPD Equipment with DET TID-1 Ion Source and DET Current Supply.
All Labeled Peaks are Saturated FAME Compounds. Biodiesel Fuel Sample was
made from Recycled Restaurant Frying Oils. Peaks 12 and 16 are Palmitic and
Stearic FAMES, respectively. Peaks 8, 23, 31, and 36 are other saturated FAMES.

Table 1. Concentrations in wt% of Fatty Acid Methyl Ester compounds in FAMES sample. Solvent: Methylene Chloride. (Supelco mix #47885-U).

- 1.) Butyric (C4:0), 4wt%;
- 2.) Caproic (C6:0), 4wt%;
- 3.) Caprylic (C8:0), 4wt%;
- 4.) Capric (C10:0), 4wt%;
- 5.) Undecanoic (C11:0), 2wt%;
- 6.) Lauric (C12:0), 4wt%;
- 7.) Tridecanoic (C13:0), 2wt%;
- 8.) Myristic (C14:0), 4wt%;
- 9.) Myristoleic (C14:1), 2wt%;
- 10.) Pentadecanoic (C15:0), 2wt%;
- 11.) cis-10-Pentadecenoic (C15:1), 2wt%;
- 12.) Palmitic (C16:0), 6wt%;
- 13.) Palmitoleic (C16:1), 2wt%;
- 14.) Heptadecanoic (C17:0), 2wt%;
- 15.) cis-10-Heptadecenoic (C17:1), 2wt%;
- 16.) Stearic (C18:0), 4wt%;
- 17.) Oleic (C18:1n9c), 4wt%;
- 18.) Elaidic (C18:1n9t), 2wt%;
- 19.) Linoleic (C18:2n6c), 2wt%;
- 20.) Linolelaidic (C18:2n6t), 2wt%;
- 21.) γ -Linolenic (C18:3n6), 2wt%;
- 22.) α -Linolenic (C18:3n3), 2wt%;
- 23.) Arachidic (C20:0), 4wt%;
- 24.) cis-11-Eicosenoic (C20:1n9), 2wt%;
- 25.) cis-11,14-Eicosadienoic (C20:2), 2wt%;
- 26.) cis-8,11,14-Eicosatrienoic (C20:3n6), 2wt%;
- 27.) cis-11,14,17-Eicosatrienoic (C20:3n3), 2wt%;
- 28.) Arachidonic (C20:4n6), 2wt%;
- 29.) cis-5,8,11,14,17 Eicosapentaenoic (C20:5n3), 2wt%;
- 30.) Heneicosanoic (C21:0), 2wt%;
- 31.) Behenic (C22:0), 4wt%;
- 32.) Erucic (C22:1n9), 2wt%;
- 33.) cis-13,16-Docosadienoic (C22:2), 2wt%;
- 34.) cis-4,7,10,13,16,19-Docosahexaenoic (C22:6n3), 2wt%;
- 35.) Tricosanoic (C23:0), 2wt%;
- 36.) Lignoceric (C24:0), 4wt%;
- 37.) Nervonic (C24:1n9), 2wt%.